REMARKS/ARGUMENTS

Reconsideration is respectfully requested of the Official Action of April 14, 2005, relating to the above-identified application.

The objections to the claims are believed to be overcome by the foregoing amendments.

The rejection of Claim 20 under 35 U.S.C. § 112 (second paragraph) as indefinite is traversed and reconsideration is requested in view of the foregoing amendment which addresses the issue raised in the Official Action on page 3.

The claims in the case are 1-8, 10 and 12-21.

The indication by the Examiner that Claims 14 and 20-22 would be allowable if rewritten in independent form is noted with appreciation. In the Interview Summary Form of December 10, 2004, it was indicated that Claim 11 would also be allowable. The features of Claims 9 and 11 have been inserted into Claim7 and, therefore, it is believed that Claim 7 has been placed in condition for allowance. Dependent Claims 8, 10, 12-21 are now all dependent on Claim 7 and, accordingly, applicants believe that these claims are now also in condition for allowance.

The rejection of Claims 1 and 3-6 under 35 U.S.C. § 102(b) as anticipated by the European Patent Application No. 0 724 968 is traversed and reconsideration is respectfully requested.

The Final Action refers to the Office Action of December 1, 2004, which summarizes the cited European patent reference as describing a pigment-dye combination ink formed by mixing a pigment ink containing a carbon black dispersion with a water soluble dye ink B. The Final Action states that "furnace black and channel black are all examples of gas black". The IUPAC document has been made of record in the Final Action. Applicants have already made of record

a copy of literature from Cabot Corporation which identifies the Mogul L as a furnace black

which is the material shown in the EP document.

As further evidence to show that not all carbon blacks are the same, there is made of

record herein the following documents:

Exhibit 1.   Publication by Degussa AG (assignee herein) entitled:
              What is Carbon Black?

Exhibit 2.   Technical Bulletin: *Pigments: Properties of Pigment
              Blacks and Methods for Their Characterization* (also
              published by assignee)

Exhibit 1 shows the various methods of producing carbon black and discusses the

properties of the products. The table on page 33 compares the several different blacks and

clearly shows that the properties of the carbon blacks depend upon the method of manufacture.

Exhibit 2 shows, on page 5, the different processes for making gas black, furnace black

and lampblack. Of particular interest is Figure 3 on page 8 showing the extremely narrow

primary particle distribution compared to the other two blacks. Gas blacks (of the present

invention) also have a high structure; see page 13. Note further the differences in surface

chemistry as explained on page 19. Other points of distinction between gas blacks and other

forms of carbon black are highlighted for the convenience of the Examiner.

In view thereof, applicants respectfully submit that persons skilled in the art would know

that gas blacks are not identical to furnace blacks or any other carbon blacks described in the

cited references. Therefore, it appears clear that the cited reference fails to describe the claimed

invention. Accordingly, the rejection under 35 U.S.C. § 102 should be withdrawn.

The rejection of Claims 2, 7, 8, 10, 12, 13 and 15-19 as allegedly obvious (35 U.S.C. § 103), in view of the European document, is also traversed and reconsideration is respectfully requested.

With regard to the allegation in the Official Action that a person skilled in the art would be lead to substitute any gas black for the carbon black produced by the furnace process or the channel process, applicants would respectfully disagree and note that there is no teaching or allegation that any other type of carbon black would be suitable. There is no motivation to select a gas black from among the many types of carbon blacks that are available, nor would there be any predictability as to success. The record establishes that not all carbon blacks are the same and further that the industry makes clear distinctions with respect to the variety of carbon blacks.

Consequently, applicants respectfully submit that there is lacking a motivation in the European document whereby a person skilled in the art would be lead to substitute a gas black for the carbon blacks shown in the reference.

For reasons set forth herein, applicants respectfully submit that the rejection fails to establish *prima facie* obviousness and should be withdrawn.

Respectfully submitted,

SMITH, GAMBRELL & RUSSELL, LLP

By:_____

Robert G. Weilacher, Reg. No. 20,531

Suite 3100, Promenade II
1230 Peachtree Street, N.E.
Atlanta, Georgia 30309-3592
Telephone: (404): 815-3593
Facsimile: (404): 685-6893

LIT\913655.1

Technical Bulletin Pigments

*Properties of pigment blacks
and methods for their characterization*

Number 14

Printex 9
Printex 30
Printex V
Printex U
ntex 150 T
Printex 200
Printex 35
Printex 300
Printex 140 U
Printex A
Printex 85
Printex 60
Printex 80
ntex G
Special Black 250
Printex XE 2
Colour Black FW 200
Special Black 6
cial Black 4 A
Colour Black S 160
Special Black 100
Colour Black FW 1
al Black 550
FW 18
lour Black S170

degussa

Contents

1. Introduction

Pigment blacks are produced on an industrial scale by incomplete combustion or by the thermal decomposition of hydrocarbons under strictly defined conditions. Degussa-Hüls is the only carbon black manufacturer using three different processes for the production of pigment blacks:

- the furnace black process,
- the gas black process,
- the lampblack process.

This results in a very wide range of extremely different pigment black types, which permits the various requirements of the market to be satisfied.

In order to characterize the pigment blacks and in order to control the carbon black production process, numerous testing methods have been developed. The properties which pigment blacks impart to printing inks, paints, plastics and other special applications can be traced back to the following fundamental properties of the pigment black itself:

- particle size and surface area
- porosity
- structure
- surface chemistry.

The purity of the pigment blacks also plays an important part, as do further properties which relate to the physical form, the handling and the ability of the pigment blacks to be processed. These physico-chemical properties can be set in a deliberate way via the raw material, the production process and the production conditions, as well as by oxidative and mechanical after-treatment processes.

However, the knowledge of the physico-chemical properties is not sufficient to be able to describe the application behavior of pigment blacks, since the efficiency of a pigment black also depends, for example, on the degree of dispersion achieved in a system. Instead, application test methods have also had to be developed for the demands of the most diverse application sectors.
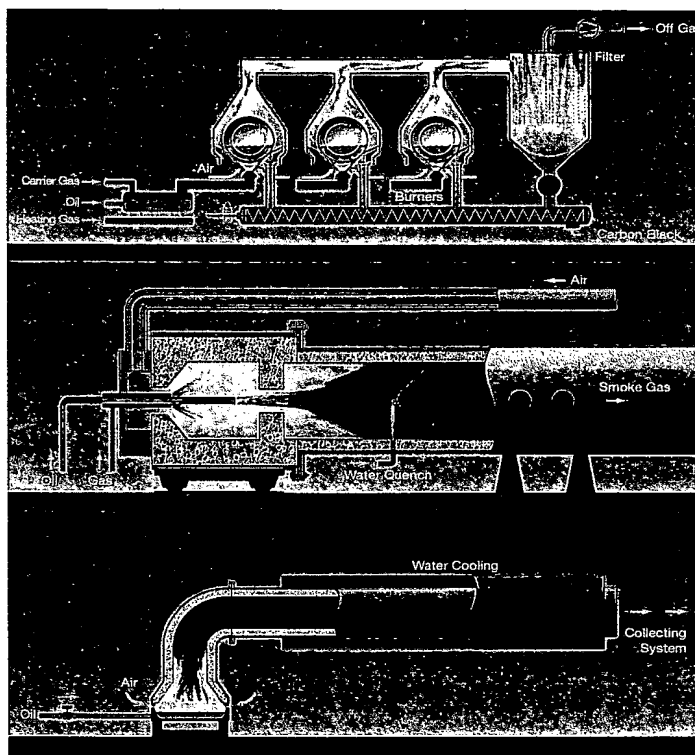
Figure 1: Processes for producing pigment blacks: Degussa-Hüls gas black, furnace black and lampblack processes (from top to bottom)

Pigment blacks are obtained in continuous processes. It is therefore not possible to set exactly defined properties as in a batch process. The continuous method of production necessarily leads to products whose properties fluctuate within certain ranges. In order to keep these deviations within very narrow limits, the production units are controlled in accordance with the SPC (statistical process control) rules. Some important characteristics are determined at regular intervals during the production process and are used not only for process control but also permit the uniformity of the production to be assessed. The "Capability Indices" Cp and Cpk are used to check the severity of scatter of the measured values.

2. National and International Standards

A large proportion of the carbon black characteristics are determined in accordance with standardized test methods, which have been elaborated by the Deutsche Institut für Normung e.V. (DIN), the International Organization for Standardization (ISO) and the American Society for Testing and Materials (ASTM), and have been defined as mandatory.

In many cases, however, these standards are specifically tailored to wet-beaded rubber carbon blacks, so that these testing methods have had to be adapted to the requirements of pigment blacks. Beyond it, Degussa-Hüls is continuing to develop new test methods for different applications.

Table 1: National and international test methods

Test Method	DIN, ISO, DIN EN ISO	ASTM-D	Degussa-Hüls Properties	Methods
Methods for determining the surface area				
Determining the iodine absorption	DIN 53582, ISO 1304	1510	713/R037	713/R006
Determining the nitrogen surface area	DIN 66131/2, ISO 4652	3037/4820	713/A004	713/A014
Determining the CTAB surface area	ISO 6810	3765	713/R036	713/R018
Statistical thickness surface area		5816		
Methods for determining the structure				
Determining the DBP absorption	DIN 53 601, ISO 4656	2414	713/R008	713/R012
Determining the CDBP absorption	ISO 6894	3493	713/R001	713/R017
Oil absorption (yield point method)	DIN EN ISO 787-5		713/A006	713/K055
Determining the pour density	DIN 53 600, ISO 1306	1513	713/R045	713/R007
Determining the tamped density	DIN EN ISO 787-11		713/A012	713/A002
Methods for characterizing the carbon black surface				
Determining the volatiles at 105°C	DIN EN ISO 787-2	1509	713/A013	713/A004
Determining the heating loss at 950°C	DIN 53 552		713/R026	713/R027
Determining the pH value	DIN EN ISO 787-9	1512	713/R042	713/A005
Methods for determining impurities				
Determining the ash content	DIN 53 586, ISO 1125	1506	713/R030	713/R031
Determining the sieve residue	DIN EN ISO 787-18	1514	713/A008	713/A008
Toluene extractables	DIN 53 553, ISO 6209	4527	713/R067	713/R028
Determining the total sulfur content	DIN 53 584	1619	713/A021	713/A012
Determining the electrical resistivity of aqueous pigment extracts	DIN ISO 787/14	–	713/R055	713/R052
Handling properties				
Determining the individual pellet crush strength	DIN 53 603	3313/5230	713/R013	713/R021
Determining the fines content	DIN 66 165	1508	713/R083	713/R029
Coloristic methods				
Determining the blackness value My of powder pigment blacks	DIN 55 979	–	713/R047	713/R035
Determining the relative tinting Strength of powder and beaded pigment blacks	DIN EN ISO 787-16/24	–	713/R018	713/R042
Determining the relative blackness value MYr and the absolute contribution of hue dM of powder and beaded pigment blacks in an alkyd/melamine resin baking enamel	–	–	713/R043 713/R019	713/R025

The Degussa-Hüls test methods listed in Table 1 are obtainable as individual printed texts on request.

The list reflects the current status and is continuously updated and supplemented.

3. Cataloguing Data

Cataloguing data from various institutions have been compiled in Table 2; these data facilitate the material registration and characterization of the pigment blacks. In the "Raw Materials Handbook, Volume 4, Pigments" from the National Printing Ink Research Institute (NPIRI), inorganic pigments, also including pigment blacks, are classified by type, color-fastness and resistance to chemicals.

Table 2: Cataloguing data

Institution	Furnace black, Gas black	Lampblack
CAS (Chemical Abstracts Service) Registry number	1333-86-4	
MITI (Ministry of International Trade and Industry Japan) Section/Class Reference number	3074/10/5-3328	3073/10/5-5222
EINECS (European Inventory of Existing Commercial Chemical Substances) number	2156-099	
ECI (Existing Chemicals Inventory, Korea) number	6-306, 5-1772	
Colour-Index Number (Association of Colour Chemists, USA und GB)		
Chemical Class	Inorganic	Inorganic
Colour index generic name	Pigment black #7	Pigment black #6
Colour index constitution number	77266	77266
Fastness data		
Organic solvents	Insoluble	
Light	Excellent	
Heat	Excellent	
Water	Insoluble	
Sodium carbonate solution 5%	Unchanged	
Hydrochloric acid 5%	Unchanged	
Linseed oil	Insoluble	
Oleic acid	Insoluble	
NPIRI, Raw Materials Handbook, Volume 4, Pigments		
Fastness data		
Water (20°C, 100 °C, process steam sterilization)	No bleed or discoloration	
Acid (hydrochloric acid 5%, lactic acid 3%, acetic acid 2%)	No bleed or discoloration	
Alkali (sodium hydroxide 2%, sodium carbonate solution 5%)	No bleed or discoloration	
Organic solvents (non-polar, polar)	No bleed or discoloration	
Chemicals (plasticizers, oils, fats, greases, hot wax, soap)	No bleed or discoloration	
Color permanency		
Indoor: lightfastness in a carbon arc or xenon lamp fadeometer	No bleed or discoloration	
Outdoor: Weathering tests in Florida	No bleed or discoloration	
Baking stability: Temperature range from 90 to 200°C	No bleed or discoloration	

The predominant property of pigment black is its excellent resistance to water, acids, alkali, organic solvents and other chemicals. The action of light and the influence of weather and temperature do not lead to any impairment of the coloristic properties.

The limiting factor in this case is generally not the pigment black itself but rather the binder system in which the pigment black was embedded for the investigations. The data were determined on a dried paint film.

4. Pigment Black Properties

4.1 Primary Particle Size

Only through the development of the electron microscope in the thirties did it become possible to make the primary particles of pigment blacks (Figure 2) visible. Pigment black consists of approximately spherical particles, the so-called primary particles, which have grown together to form three-dimensionally branched aggregates, as is typical for products which have been produced from the gas phase. The level of aggregation is also referred to as the "structure" of the carbon black.

By means of measuring and counting the individual primary particles, using the semi-automatic particle-size analyser from Carl Zeiss or using a computer-aided image analysis system, it is possible to determine not only the average primary particle size but also the primary particle size distribution. Figure 3 shows primary particle size distributions of the gas black grade FW1, the furnace black grade Printex 3 and the Lampblack 101. Gas blacks exhibit a very narrow distribution, while lampblack has a very wide distribution. Furnace blacks assume a middle position in this case.

Depending on the average primary particle diameter, which may lie between 5 and 500 nm, the pigment blacks are subdivided into four groups: High Color (HC), Medium Color (MC), Regular Color (RC) and Low Color (LC), reference being made to the process (F = Furnace black process, C = Channel black or Gas black process) by a further letter. Table 3 shows the subdivision of the furnace and gas blacks into these four groups.

In the furnace black process, the average particle size can be varied between 10 and 80 nm; in the gas black process it can be varied between 10 and 30 nm. Lampblack 101 has an average primary particle size of 95 nm.

4.2 Microstructure

Using a high-resolution electron microscope, it is even possible to make details of the carbon black particles, the microstructure of the pigment black, visible. In combination with X-ray structural analysis, it is possible to demonstrate that these primary particles consist of graphite-like crystallites which are arranged co centrically and have grown with one another, the mutually parallel layers often being offset laterally and rotated axially (turbostratic structure, Figure 4). These basic structural units (BSUs) have an L_a value of 1.5-2.5 nm and an L_c value of 1.0-1.5 nm, which corresponds to 3–4 carbon layers each having 30–90 six-membered carbon rings.
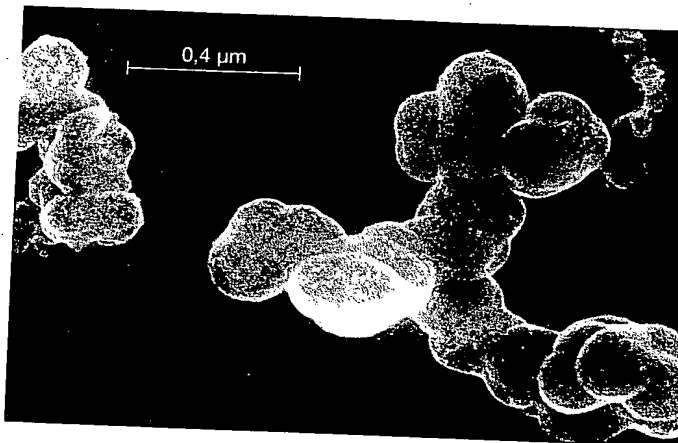

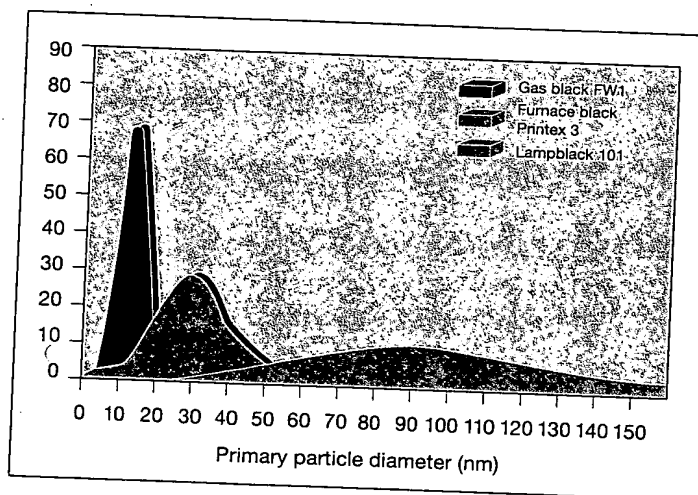Figure 2: Scanning electron micrograph of a lampblack aggregate

Figure 3: Primary particle size distributions of different pigment blacks

Table 3: Classification of pigment blacks by jetness and average primary particle size

Designation	Average Primary Particle Size
HC(F,C)	10 – 15 nm
MC(F,C)	16 – 24 nm
RC(F,C)	25 – 35 nm
LC(F)	> 35 nm

The spacing between the graphite layers, as compared with graphite has been increased slightly from 3.35 Å to 3.5 Å. A primary particle with a diameter of 20 nm contains about 400,000 carbon atoms.

However, high-resolution TEM phase-contrast images have shown that the primary particles do not consist of a collection of isolated crystallites but that they have a "paracrystalline" structure. Accordingly, the hexagonal graphite layers are much larger than just the base areas of the crystallites determined by X-ray diffraction; they extend over further regions and must therefore be curved. They produce the bonding between the crystallites and the aggregated primary particles, which is significant for the electrical conductivity of pigment blacks (Figure 5).

More recent results from scanning tunnel microscopy lead in the same direction, and permit one to suppose that the primary particles are built up of graphite layers which are superimposed like roof tiles. Therefore, the L-values determined by means of X-ray diffraction must be viewed as the average overlap area of graphite layers and not as the average size of independent crystallites.

Apart from transmission electron microscopy (**TEM**), scanning electron microscopy (**SEM**) and scanning transmission electron microscopy (**STEM**), further high-resolution techniques were used to clarify the microstructure of the carbon black surface. With the aid of scanning tunnelling microscopy (**STM**) and scanning or atomic force microscopy (**SFM or AFM**), it is possible to achieve resolutions in the atomic range and thus make individual carbon atoms visible. In this connection, mention should also be made of ultra-small angle X-ray scattering (**USAXS**), which permit conclusions to be drawn about the surface roughness values and about the size of primary parti-cles and aggregates. New hopes have also been raised by the further development of electron microscopy which, with the aid of a correction, should permit resolutions down to 0.14 nm.

These microscopic methods have a high potential, which has still not been exhausted, and will thus make a contribution to the further clarification of the surface structure of pigment blacks.
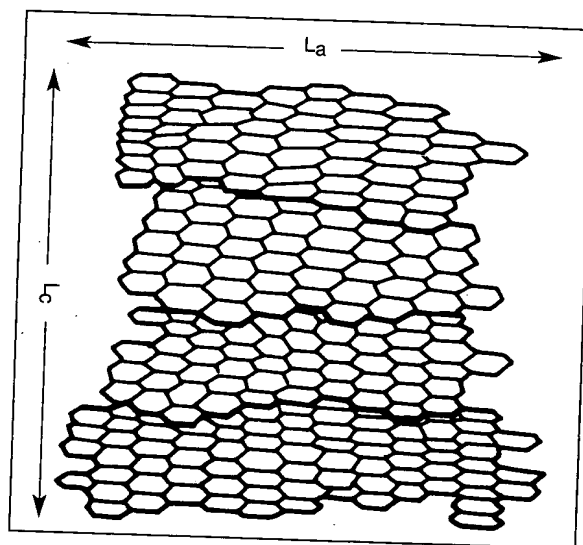

Figure 4: Structure of a carbon black crystallite of graphite-like layers (schematic)
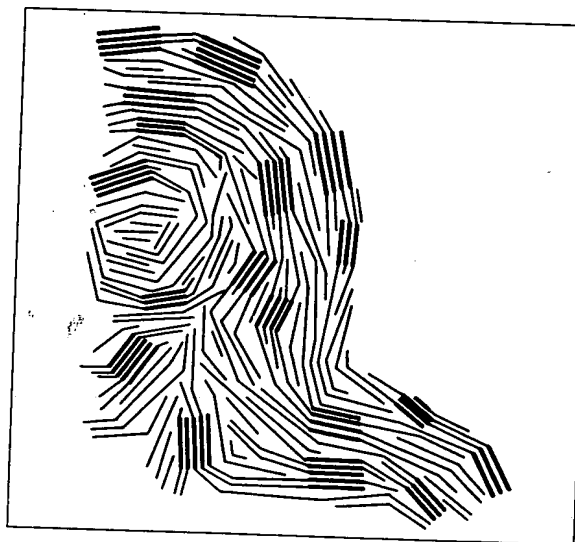

Figure 5: Paracrystalline structure of pigment black (schematic)

4.3 Surface Area

As already described under 4.1, the average primary particle size can be determined by measuring and counting the individual primary particles. On the basis of the primary particle size d_A averaged over the surface area, it is possible to calculate the so-called electron-microscopic surface area EMSA directly in m^2/g in accordance with the following formula, the carbon density ρ being assumed to be 1.86 g/ml and d_A being used in nm.

$$EMSA = \frac{6000}{\rho * d_A} = \frac{6000}{1.86 * d_A} \, [m^2/g]$$

The surface area is inversely proportional to the primary particle size, that is to say pigment blacks having smaller primary particles consequently have a greater specific surface area and vice versa. Figure 6 reproduces the graphical illustration of this relationship, in which it is possible to see that, in the case of fine-particle pigment blacks, even small changes in the primary particle size have a very considerable effect on the surface area. This sharp growth in the surface area is also the reason why pigment blacks are considerably more difficult to disperse as their degree of fineness increases.

In calculating the EMSA, spherical, isolated particles were assumed, which is not the case in reality. In addition, surface area losses because of the aggregation of the primary particles as well as the surface roughness and porosity of a pigment black are not registered.

Since electron-microscopic investigations are very costly and time-consuming and are therefore not suitable for routine measurement and for production control, a series of methods of determining the surface area of pigment blacks has been developed instead, and are based on the adsorption of defined molecules (for example nitrogen, iodine and cetyltrimethylammonium bromide (**CTAB**). However, the disadvantage of this process is that each method results in "its specific surface area" and that these surface area values do not contain any information relating to the primary particle size distribution.

The most common methods are:

• BET surface area,
• iodine adsorption,
• CTAB surface area,
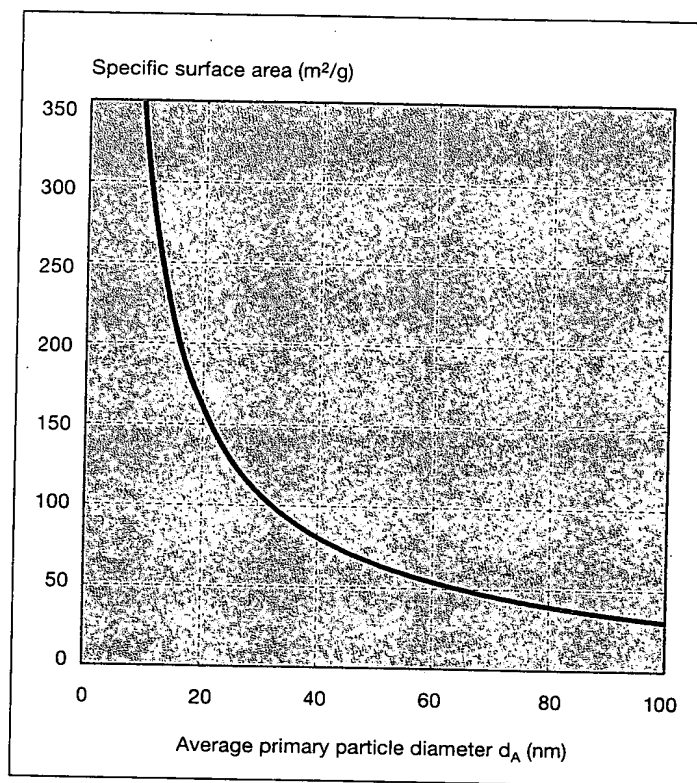• statistical thickness surface area (**STSA**).

Figure 6: Specific surface area EMSA as a function of the average primary particle size d_A

4.3.1 BET Surface Area

In order to determine the BET surface area, nitrogen is generally used. At the boiling point of liquid nitrogen (–196°C), the pigment black is completely loaded with nitrogen. From the desorption curve in the relative pressure range p/p_0 from 0.05 to 0.3 (p_0 = saturation vapour pressure of the boiling nitrogen) it is possible to calculate the nitrogen volume needed for a monolayer coverage in accordance with the BET theory of Brunauer, Emmett and Teller. Given a surface area requirement of a nitrogen molecule of 0.162 nm^2, one obtains the specific surface area of the pigment black in m^2/g.

In the case of non-porous pigment blacks, the BET surface area agrees well with the EMSA. This is initially surprising, since the overlap areas of the aggregate primary particles are not accessible to nitrogen and therefore lower values should be found. Apparently, this effect is compensated for by the surface roughness of the carbon black particles. In the case of porous pigment blacks, considerably higher values are obtained, as compared with EMSA, since the very small nitrogen molecule can penetrate into pores
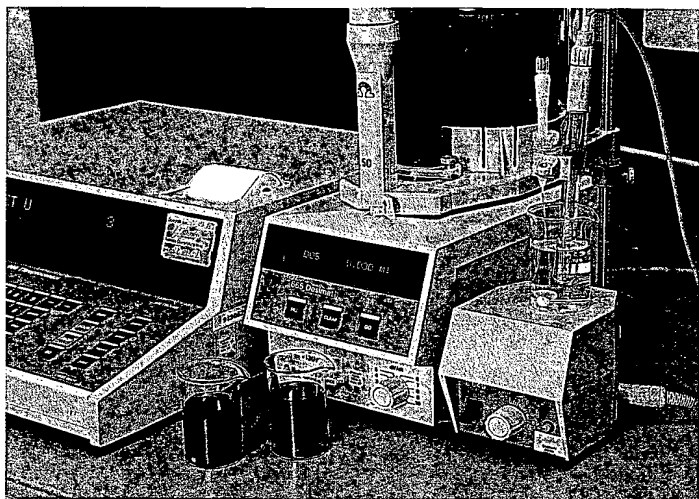
Figure 7: Potentiometric determination of the iodine adsorption. Left: aqueous iodine solution, Centre: following the addition and separation of the pigment black, Right: after the end point has been reached.

and gaps in the carbon black particle, and the internal surface area is registered at the same time.

The BET surface area therefore contains the external and internal surface area and is a measure of the total surface area of the carbon black particles. The measurement is not influenced by surface oxides and hydrocarbon residues on the surface of pigment blacks.

4.3.2 Iodine Adsorption

Iodine adsorption is certainly the method which is most frequently used to determine the surface area. This is a rapid method which can also be used for production control. The iodine adsorption number can be calculated from the adsorption of iodine from an aqueous iodine solution, is specified in mg of adsorbed iodine per gram of pigment black and therefore does not represent a true surface area. However, the concentration of the iodine solution is selected in such a way that, in the case of non-porous pigment blacks, these values agree in purely numeric terms with the BET surface area. One therefore also speaks of "iodine surface area", but without converting the values into m²/g.

The iodine adsorption also registers the internal surface area of the carbon black particles. However, by comparison with the BET measurement, only part of the porosity is registered, since the iodine molecule is considerably larger than the nitrogen molecule and cannot penetrate into the finest pores (< 0.4 nm).

However, a decisive disadvantage of this method is that it is strongly influenced by organic impurities and by oxygen-containing groups on the carbon black surface. Hydrocarbon residues on the surface or mineral oils which are used for beading hamper the adsorption of iodine and therefore lead to a reduction in the iodine adsorption. Highly polar carbon black surfaces, such as are to be found in gas blacks and in oxidized pigment blacks, lead to preferred adsorption of water from the aqueous KI-I_2 solution, so that in this case, too, the resulting values are too low. The oxidation of iodide to iodine by peroxide groups on the carbon black surface likewise has the effect of depressing the iodine adsorption.

This method is therefore restricted to furnace blacks and lampblack, and does not supply any useable results for gas blacks and oxidized pigment blacks. It is possible to get around these restrictions by calcining the pigment black to 950 °C, with the exclusion of air, before the determination. In this case, however, there is the risk that additional porosity will be produced. This procedure is of no practical use.

4.3.3 CTAB Surface Area

The so-called CTAB surface area can be calculated from the adsorption of cetyltrimethylammoniumbromide from an aqueous solution. A surface area requirement of 0.44 nm² is assumed for the CTAB molecule. Because of its size, the CTAB molecule cannot penetrate into micropores (< 1.1 or 1.5 nm). The CTAB method therefore registers the smooth, external surface area of the carbon black, which is accessible to elastomers and other polymers.
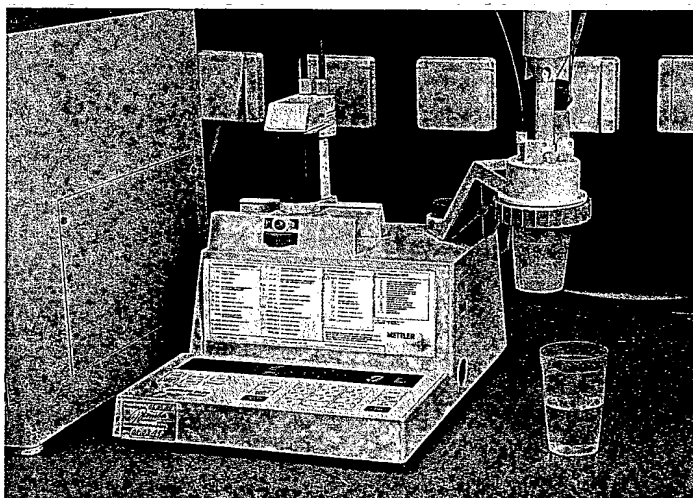

Figure 8: Photometric determination of the CTAB surface area.
Bottom: solution following the separation of the pigment black,
Top: after the end point has been reached

One therefore also finds a very good correlation between the CTAB surface area and the particle size determined by electron microscopy.

The CTAB surface area determination is not influenced by hydrocarbon residues on the carbon black surface, but also leads to elevated values in the case of highly polar surfaces, such as are to be found in gas blacks and in oxidized pigment blacks. There are also references to the fact that the measured values are influenced by densifying the carbon black.

4.3.4 Statistical Thickness Surface area

The statistical thickness surface area, like the BET surface area measurement, is based on the adsorption of nitrogen, the measurement being extended to a higher relative pressure range p/p_0 from 0.2 to 0.5. The evaluation of the adsorption isotherms via t-plots, in which the adsorbed nitrogen volume is plotted against the statistical layer thickness t of nitrogen, yields the external surface area of the carbon black particles, since the micropore surface area (pores < 2 nm) is excluded. There is, therefore, a very good correlation with the CTAB surface area, the STSA values being some 4 to 5 points lower.

The great advantage of this method is based on the fact that the measurement is influenced neither by surface oxides nor by hydrocarbon residues on the carbon black surface. If measurements are made over the entire relative pressure range p/p_0 from 0.05 to 0.5, it is even possible to determine the total surface area (BET) and the external surface area (STSA) in one measurement, and to obtain information about the porosity of pigment blacks from the difference between the two values.

4.3.5 Comparison between the different Methods of determining the Surface Area

The various methods for determining the surface area are compared with one another in Table 4.

EMSA, STSA and CTAB surface area are a measure of the external surface area and therefore exhibit a good correlation with the primary particle size. BET surface area and iodine adsorption register the internal and external surface area. The decisive advantage of the methods (BET surface area and STSA) based on the adsorption of nitrogen is their insensitivity to surface area oxides and hydrocarbon residues on the carbon black surface.

4.4 Porosity

The determination of the porosity in pigment blacks is of considerable importance from a theoretical and application point of view. A distinction is drawn between open and closed porosity. Open pores can be imagined as gaps, clefts or channels in the Ångström range, which can also serve as access pores for larger voids in the interior of the carbon black particles. As a result of severe oxidation, it is even possible for hollowing of the primary particles to occur, so that only shells remain. One speaks of closed porosity if the voids are not accessible from the surface. Particularly high porosities are found in conductive carbon blacks, very fine-particle and/or oxidized pigment blacks. By far the major part is present as open pores in the micropore range (< 2 nm).

Table 4: Methods of determining the surface area

| Method	Adsorbate	Surface Area Requirement	Pores Registered	Surface Area Registered	Limitations
EMSA				External, geometric surface area	None
BET-surface area	Nitrogen	0.14 nm²	> 0.3 nm	External + internal surface area = total surface area	None
Iodine adsorption	Iodine	0.30 nm²	> 0.4 nm	External + internal surface area = surface area	Surface oxides, hydrocarbon residues
CTAB-surface area	CTAB	0.44 nm²	> 1.1 bzw. 1.5 nm	External surface area	Surface oxides, degree of densification
STSA	Nitrogen	0.14 nm²	> 2.0 nm	External surface area	None

12
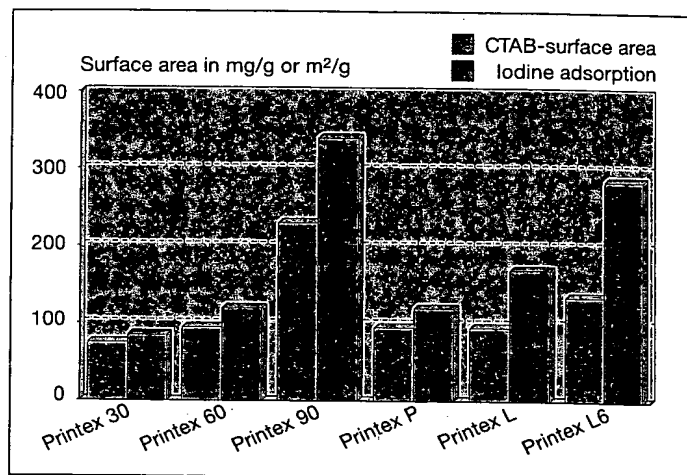
Figure 9: *Difference between iodine adsorption and CTAB surface area as a measure of the porosity*

The original methods for determining the porosity are based on density and gas-adsorption measurements. By comparing the helium density with the hydrocarbon density which is given by X-ray diffraction measurements, it is possible to draw conclusions, for example, about the closed pore volume. It is possible for pore sizes, pore volumes and pore distribution to be determined on the basis of the nitrogen adsorption isotherms, for example using the t-plot method of de Boer.

For most cases, however, it is sufficient to use, as a measure of the porosity of a pigment black, the internal surface area which is given by the difference between the total surface area (BET surface area, iodine adsorption) and the external surface area (CTAB surface area, STSA, EMSA). The iodine adsorption and the CTAB surface area are plotted in Figure 9. The difference between the two values represents the internal surface area and exhibits a good correlation with the pore surface area.

4.5 Carbon Black Structure

As already mentioned under 4.1, pigment black consists of approximately spherical particles, the so-called primary particles, which have grown together to form three-dimensionally branched aggregates. The aggregates therefore constitute the actual basic units of pigment black. High-structure carbon blacks exhibit considerable chaining or branching, in low-structure carbon blacks this aggregation is only weakly pronounced.

The result of this chaining or branching is that voids are produced between the carbon black particles. High-structure carbon blacks exhibit a high void volume, because of the very bulky character of the aggregates. In the case of low-structure pigment blacks, significantly denser packing of the particles is possible, which result in a lower void volume and a significantly higher bulk density (Figure 10). The methods most often used for measuring the carbon black structure are based on the determination of this void volume.

One restriction which should be added is that a variation in the structure is possible only in the furnace black process. In the other processes for producing pigment black, a structure which cannot be changed is established by the process. Gas blacks, lampblacks and acetylene blacks have a high structure; thermal black has a very low structure, in which even individual spherical particles are to be found. The electron micrographs in figures 11a–d show a furnace black of medium primary particle size with a high structure (a) and a low structure (b), the coarse-particle lampblack (c) and the fine-particle gas black grade FW1 (d).
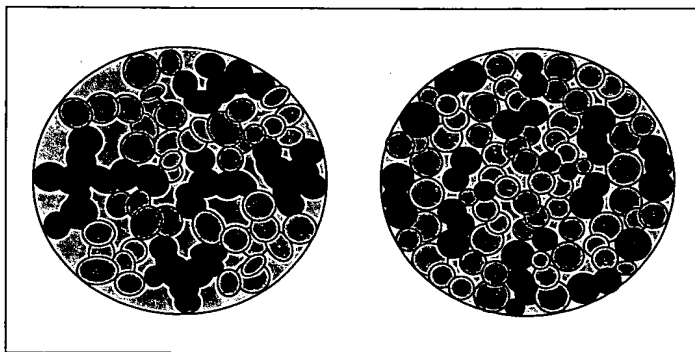

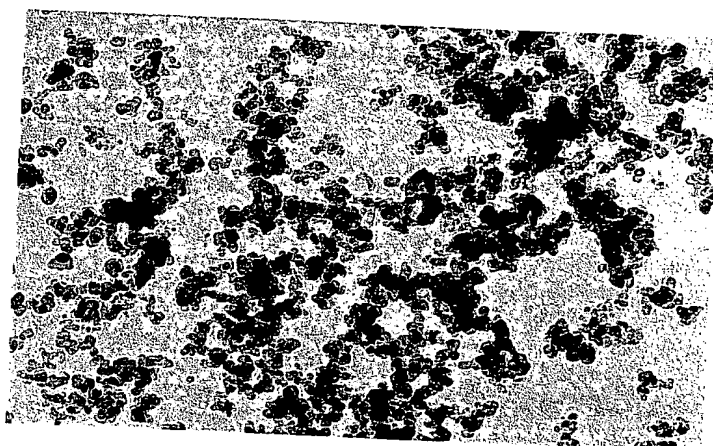Figure 10: *Pigment blacks with high and low structure (schematic)*

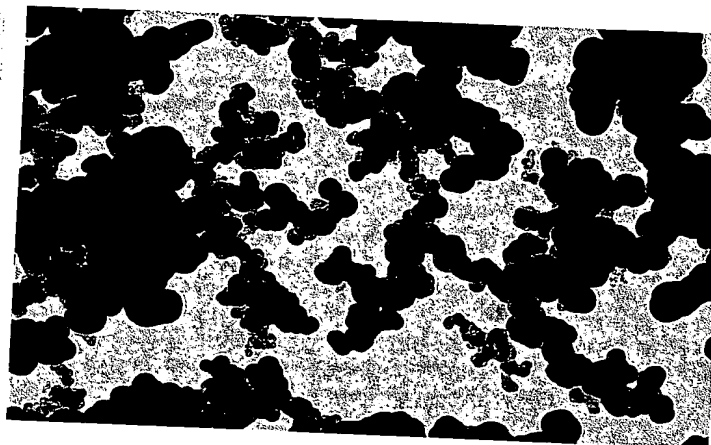*Figure 11a: Furnace black with high structure*
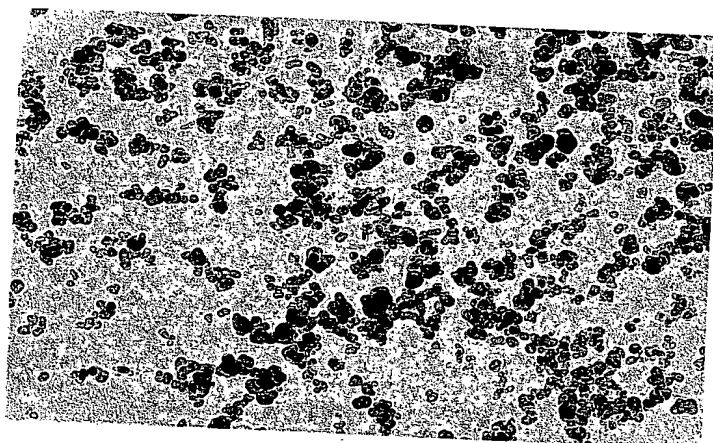

Figure 11c: Lampblack

Figure 11b: Furnace black with low structure

Figure 11d: Gas black grade FW1

A distinction is drawn between direct and indirect methods for determining the structure. Direct methods give the average aggregate size as a re-sult, indirect methods are based on the determination of the void volume between the particles.

Direct methods are

- electron microscopy,
- disc centrifuge photosedimentometry,
- photon correlation spectroscopy,
- laser diffractometry,
- Coulter counter,
- ultrasonic methods.

The **indirect methods** include

- oil absorption (flow-point method),
- DBP absorption (**DBP = dibutylphthalate**),
- CDBP absorption,
- void volume,
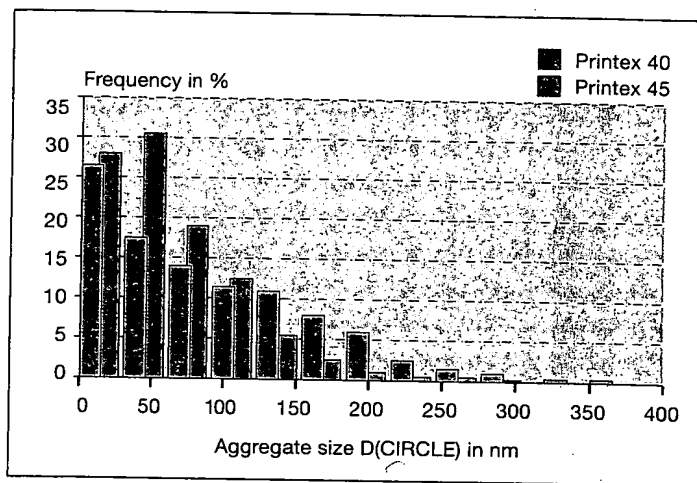- pour and tamped density.

14

Figure 12: *Aggregate size distribution of a low-structure and a high-structure pigment black*

4.5.1 Direct Methods for determining the Carbon Black Structure

4.5.1.1 Electron Microscopy

Using electron micrographs, which are evaluated by a computer-assisted image analysis system, it is possible to determine not only the primary particle size but also the aggregate size, the aggregate size distribution and the aggregate shape, the preparation of the specimen having a decisive influence on the result. In spite of the fact that the image is only two-dimensional, four different categories of aggregates can be distinguished: spherical (= discrete primary particles), ellipsoidal, linear and branched aggregates. Thermal carbon black and even very low-structure carbon blacks contain a higher proportion of isolated primary particles; in the case of fine-particle and very high-structure carbon blacks, the branched aggregates dominate.

While the statement of a primary particle diameter is unequivocal, because of the spherical symmetry, when describing aggregates one has the choice between an average minimum or maximum diameter (D_{MIN}, D_{MAX}), the diameter of a circle of equal area (D_{CIRCLE}) or else the average aggregate area (AREA) and of the average aggregate perimeter (PERIM). Figure 12 shows the aggregate size distribution of the pigment blacks Printex 40 and Printex 45 on the basis of D_{CIRCLE}.

Table 5: *Various aggregate characteristics*

Aggregate Size	Printex 40	Printex 45
D(50)$_{MAX}$	103 nm	68 nm
D(50)$_{MIN}$	59 nm	44 nm
D(50)$_{CIRCLE}$	64 nm	46 nm
AREA(50)	5235 nm^2	3941 nm^2
PERIM(50)	428 nm	322 nm

Table 5 shows the different values for the pigment blacks Printex 40 and Printex 45. As expected, the low-structure pigment black Printex 45 has considerably smaller aggregates, which is expressed both in the different diameters and in the aggregate area and in the periphery.

4.5.1.2 Measurements in the liquid Phase

As in electron microscopy, the preparation of the specimen also plays a decisive role in the methods for determining the aggregate size in the liquid phase. The result of the measurement depends directly on the level of dispersion of the carbon black particles achieved and the stabilization of this dispersion by wetting agents. A further handicap of optical measuring methods is that, because of the high light absorption capacity of pigment black, measurements are possible only on extremely highly diluted solutions. The methods which are used in the liquid phase are based on sedimentation, ultra-filtration, light scattering and ultrasound.

Photon correlation spectroscopy (PCS) is a dynamic scattered-light method in which, because of the Brownian molecular movement of the dispersed particles, the time-dependent fluctuations in the measured intensity of the scattered light are detected. It is possible to use these data to calculate an average particle size and, via the polydispersion index, a particle size distribution. The measurement range lies between 5 nm and 5 μm.

The fundamental principle of laser diffractometry (LD) is the diffraction of a laser beam, quite different diffraction images being produced on the basis of the shape and size of the particle at which the light is defracted. Using the Frauenhofer approximation or the Mie Theory, one obtains an average particle size and, via the polydispersion index a particle size distribution. The measurement range lies between 100 nm and 600 μm. In combination with polarized scattered-light measurement (PIDS) the lower limited can be reduced to 40 nm.

Of the non-optical methods, disc centrifuge photo-sedimentometry (DCP) is used very frequently. A small amount of a carbon black dispersion (1000-fold dilution) is applied to a disc. As a result of centrifugal force, the particles are separated in accordance with their size. On the basis of Stoke's Law, it is possible to calculate a diameter of a sphere (Stoke's Diameter) which corresponds to the carbon black aggregate in terms of its hydrodynamic behavior.

In the Coulter-Counter measurement principle, the detection of the particle volume is carried out on the basis of changes in the electrical resistance. Particles dispersed in the electrolyte solution are drawn through a capillary opening by applying a vacuum and, as they pass through this capillary, cause a change in the electrical resistance. The measurement range lies between 400 nm and 1200 µm and is thus less suitable for pigment blacks.

The ultrasonic methods which have been developed in recent times are very promising; in contrast with optical methods, these permit measurements to be carried out even at high carbon black concentrations.
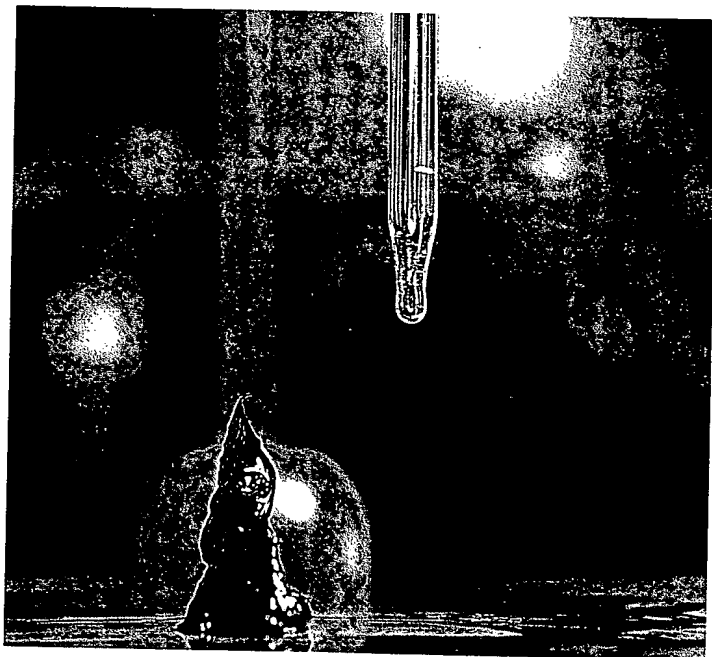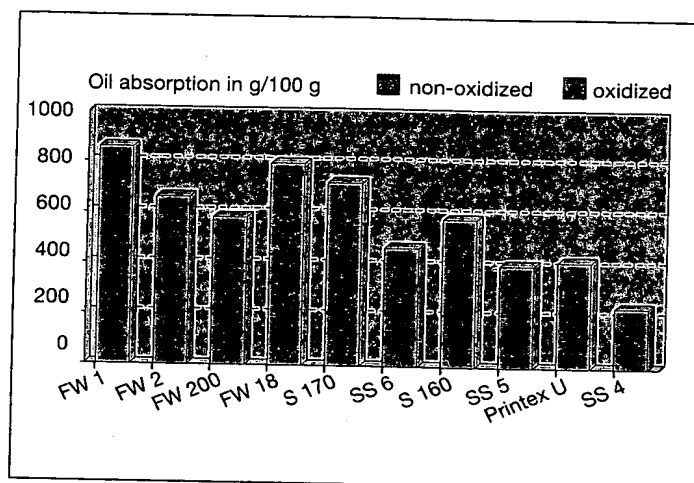

Figure 14: Oil absorption of oxidized and non-oxidized gas blacks of different primary particle sizes

4.5.2 Indirect Methods for determining the Carbon Black Structure

Indirect measuring methods do not determine the aggregate size directly, but rather the void volume between the individual carbon black aggregates and carbon black agglomerates. Available for this purpose are adsorption measurements (oil absorption, DBP) or volumetric measurements (void volume) under defined pressure conditions. Small void volumes indicate a low degree of aggregation, high void volumes indicate a bulky structure and a high degree of aggregation.

4.5.2.1 Oil Absorption (Yield Point Method)

In the determination of the oil absorption, all the pores between the carbon black particles are filled with oil. The end point of oil absorption is reached when the tip of the paste drawn up into a cone tips slightly to the side as a result of a gentle tap against the glass plate, but the paste does not yet run away completely (Figure 13).

However, the oil absorption does not depend only on the structure of the pigment black but is also influenced by the particle size, the level of densification of the pigment black and the surface groups (Figure 14). In practice, a high oil absorption also means a high binder adsorption.

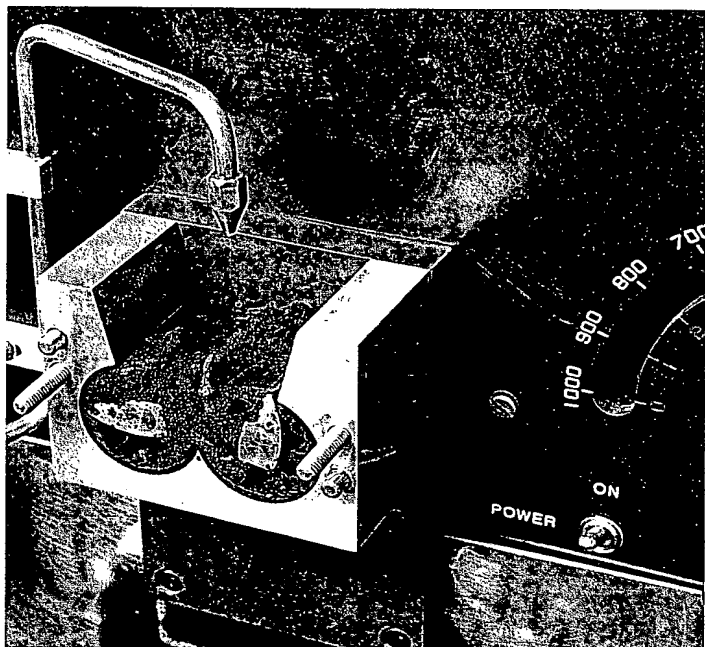Figure 13: End point of the oil absorption of a gas black found by the "yield point" method

Figure 15: Pigment black after the end point has been reached
during the determination of the DBP absorption
(detailed photograph of an open kneading chamber)

Traditionally, the determination of the oil absorption is still used in the case of gas blacks, since the DBP absorption (see 4.5.2.2) does not give any reproducible results in the case of gas blacks.

4.5.2.2 DBP Absorption

The absorption of dibutylphthalate is certainly the most widespread method for determining the carbon black structure. Pigment black is put into the kneading chamber of a measuring kneader and DBP is added. The end point has been reached when all the voids between the pigment black aggregates and agglomerates have been filled with DBP. At this point, the freely flowing powder changes into a semi-plastic compound, which causes an abrupt rise in the viscosity and in the torque (Figure 15).

The roughness of the kneading chamber has a decisive influence on the measurement result as does the wetting behavior of the pigment black and the temperature at which the measurement is carried out.

Pigment blacks are subdivided into three categories (Table 6) depending on their DBP absorption.

Table 6: Subdivision of the pigment blacks by their DBP absorption

Carbon black Structure	DBP-Absorption in ml/100g	Examples
Low	< 60	Printex 25, 35, 45, 55, 75, 85, 95
Medium	60 bis 90	Printex 300
High	> 90	Printex 30, 40, 60, 80, 90, A, G, L, L6, P, Alpha

4.5.2.3 CDBP Absorption

With the C (rushed) DBP absorption, which is also referred to as the 24M4 number, the aim is to simulate the build-up of the structure which occurs during the incorporation of a pigment black in plastic or in other binder systems. By means of the mechanical shear forces which act, "weak" aggregates and agglomerates are broken down. Before the normal DBP measurement, the pigment black is therefore compacted a total of four times in a cylinder at 165 MPa (24,000 psi), the lumps of carbon black which are produced between the individual pressings being reduced in size again and again.

A comparison between DBP and CDBP gives an indication of the stability of the aggregate structure (Figure 16). In high-structure carbon blacks (Printex 3, Printex 30 and Lampblack 101), very large differences occur between DBP and CDBP, whereas in the case of low-structure carbon blacks (Printex 300 and 35) virtually no differences are to be found.
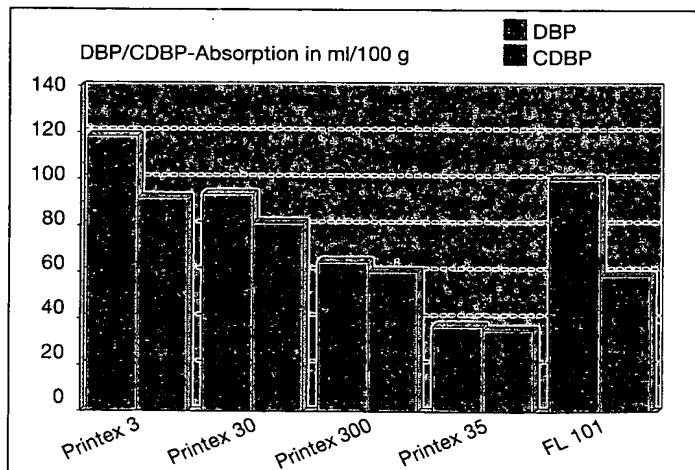

Figure 16: Comparison between DBP and CDBP absorption

These methods have great significance for the rubber sector, where very high shear forces prevail when the carbon black is being mixed in. In the pigment black sector, this method has not become widespread, since high shear forces of this type are not reached in pigment black applications.

4.5.2.4 Void Volume

A further possibility of determining the void volume between the carbon black particles is based on the compressibility of the pigment black. Pigment black has different pressures applied to it in a cylinder, and this leads to a reduction in volume. Over a wide range of pressures, the specific volume (cm³/g) exhibits a linear dependence on the logarithm of the pressure.
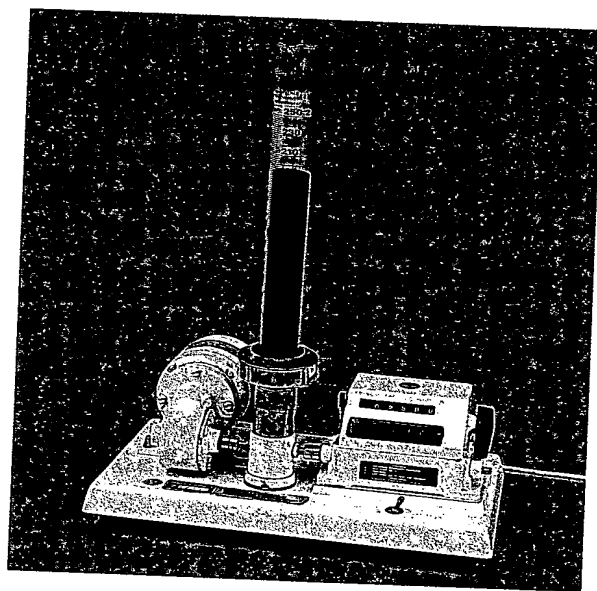
Figure 17: Apparatus for determining the tamped density

The intercept at 0.007 MPa (1 psi) gives an indication of the void volume in the virtually uncompressed pigment black, while the slope shows very good correlation with the oil absorption. High-structure carbon blacks, as expected, exhibit the highest specific volume at a given pressure and the sharpest decrease as the pressure increases. The method has not become widespread in the carbon black industry.

4.5.2.5 Pour and Tamped Density

As in the specific volume, the structure of the pigment black is also reflected in the specific density. Low-structure carbon blacks have a low void volume and therefore have a high pour or tamped density (in the case of the tamped density, a defined densification of the pigment black is carried out in a tamping volumeter, Figure 17). The converse is true for high-structure carbon blacks, that is to say the pour density is a first indication of the structure of a carbon black. However, it must be taken into account that, as the primary particles become smaller at constant structure, the pour density decreases, and that beaded carbon blacks have a distinctly higher pour density than powder carbon blacks.

This may be shown by the beaded versions of the pigment black grades Printex 3/30/300/35, Printex 40/45, Printex 80/85 and Printex 90/95 (Figure 18).

In addition, the pour density is an extremely important characteristic for the necessary volume requirement of pigment blacks during transport, as well as in the design of silo installations and volumetric metering systems.
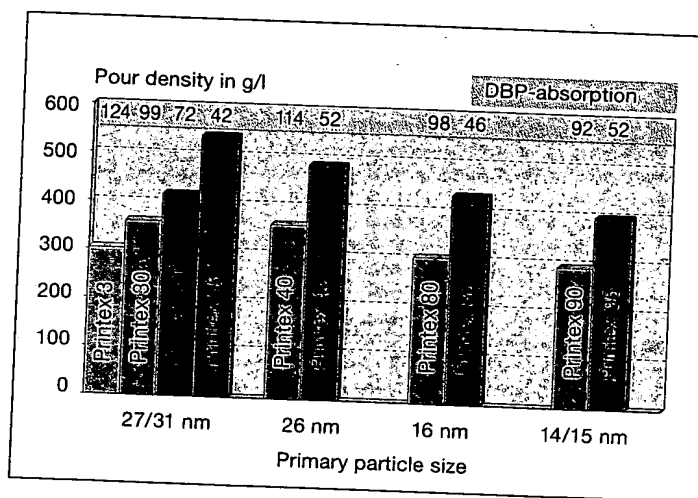

Figure 18: Relationship between structure, primary particle size and pour density

4.6 Surface Chemistry

As shown in Figure 5, the primary carbon black particles consist of graphite-like crystallites which have grown with one another. The fracture edges of these microcrystalline regions have a series of free C valencies, which are partly neutralized by hydrogen atoms. At the latest when the pigment black comes into contact with air, the remaining defects react with oxygen, forming oxygen-functional groups on the carbon black surface.

This is also the reason why the pigment blacks produced by different manufacturing processes differ sharply in terms of their surface chemistry. Gas blacks already come into contact with air at high temperatures, as a result of which mainly acid surface groups are formed. On the other hand, only a few surface oxides are to be found on the surface of furnace blacks, and these exhibit a predominantly basic character, since these carbon blacks come into contact with air only at very low temperatures.

By means of oxidizing after-treatment it is possible to increase the number of acid oxides sharply, both in gas blacks and in furnace blacks. These oxides increase the polarity and hence the hydrophily of the carbon black surface, which leads to an improvement in the wettability and to a reduced binder requirement.

Analytically, it is possible to demonstrate the following surface groups on the carbon black surface:

Carboxyl groups, lactol groups, phenol groups, quinone groups and basic oxides, for which pyrone-like structures are discussed (Figure 19). In addition, oxygen is also present on the carbon black surface as "neutral" oxide, for example in the form of ether groups.

The surface oxides differ in terms of their thermal stability. Acid functional groups split off in the temperature range from 300– 800 °C in a vacuum or in an inert gas atmosphere. Neutral surface oxides, which may be present, for example, in the form of ether-like structures, begin to decompose in the temperature range from 500–600 °C. The basic surface oxides are very stable and are broken down only at temperatures greater than 900 °C. At low temperatures, CO_2 and H_2O are formed as decomposition products; at high temperatures, CO and H_2 are produced to a greater extent.

Methods for **characterizing the surface** are

- heating loss at 950 °C,
- titrimetric determination of acid and basic surface oxides,
- pH value,
- volatiles at 105 °C,
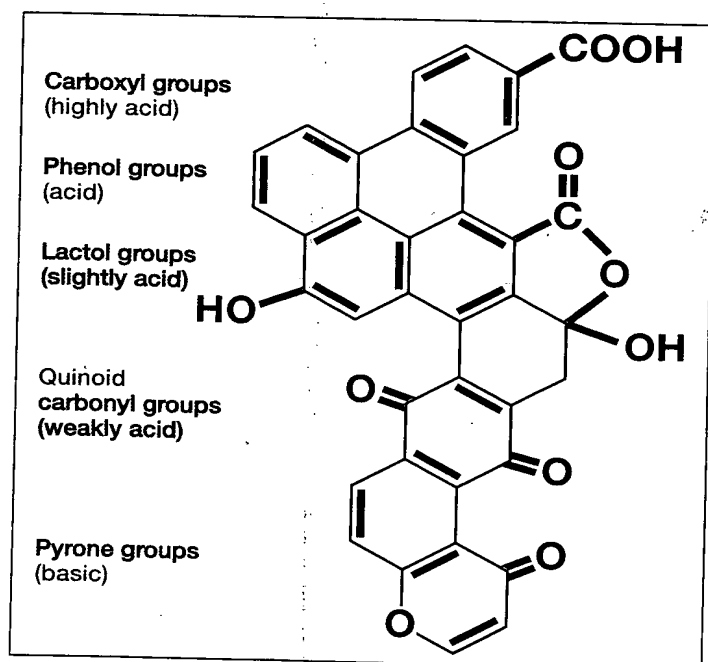- spectroscopic or spectrometric methods.

Carboxyl groups
(highly acid)

Phenol groups
(acid)

Lactol groups
(slightly acid)

Quinoid carbonyl groups
(weakly acid)

Pyrone groups
(basic)

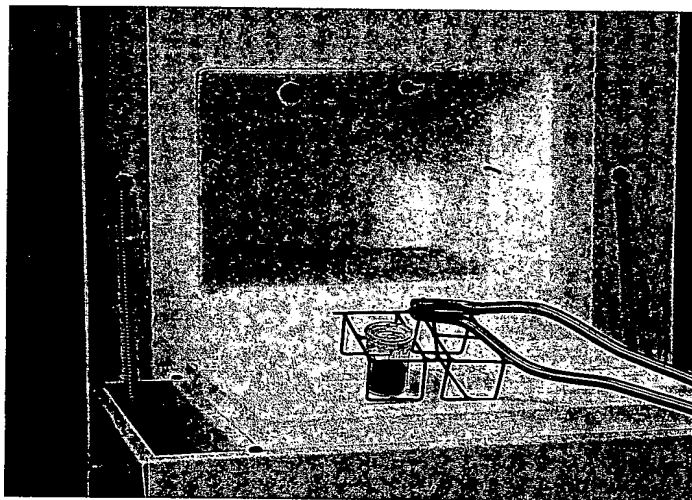*Figure 19: Oxygen-functional groups on the carbon black surface*

Figure 20: Determination of the heating loss at 950°C in a muffle furnace

4.6.1 Heating loss at 950 °C

One measure for the sum of the functional groups on the carbon black surface is the content of "volatiles", which is represented by the loss of weight of the carbon black sample when heated to 950°C for 7 minutes (Figure 20). In the case of furnace blacks, the volatiles content is <1.5%, on the other hand in the case of gas blacks it lies in the range from 4 to 6%. As a result of after-oxidation, the volatiles content can be raised to >20% in the case of gas blacks.

4.6.2 Quantitative Determination of Acid and Basic Surface Oxides

By means of a staged base titration using sodium hydrogen carbonate, sodium carbonate, sodium hydroxide solution and sodium methylate, the oxygen functional groups may be subdivided by their acidity into four groups of different acid strengths and registered quantitatively.

It is also possible to detect basic oxides on the carbon black surface by adding acid. Neutral oxygen groups, for example ether groups, are understandably not registered, but make up a significant proportion. In the case of the gas black grade FW 200, which has an oxygen content of about 16%, it is possible to explain only about half of the oxygen in terms of acid and basic surface oxides.

Using the example of the gas black grades FW1, FW2 and FW 200, it is possible to demonstrate that, as the degree of oxidation increases, the very acidic carboxyl groups and the very weakly acidic quinone groups increase, while the phenol group content passes through a maximum (Figure 21).

In the case of the furnace blacks, the basic oxides dominate. With increasing primary particle size – as in the case of the gas blacks – a considerable increase in the sum of the surface oxides can be established. In the case of lampblack, the basic and acidic oxides balance each (Figure 22).

The occurrence of the different surface groups could also be demonstrated spectrometrically by means of X-ray photoelectron spectrometry (XPS).
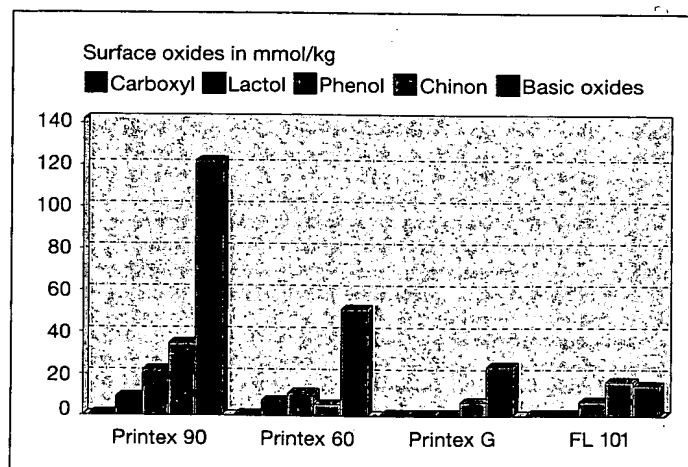

Figure 21: Oxygen functional groups of gas blacks

Figure 22: Oxygen-functional groups of furnace blacks and lampblack

4.6.3 pH Value

The pH value of a pigment black, which is determined in an aqueous pigment black suspension, permits a statement relating to the acidity of the surface groups. Low pH values point to acidic groups, high pH values to basic groups. Gas blacks have pH values around 4, in the case of oxidized gas blacks, the values lie between 2 and 3. The basic reaction of furnace blacks can be traced back to the presence of basic oxides and to alkali compounds which are used in order to adjust the structure in the manufacturing process. Oxidized furnace blacks have pH values from 3 to 4. Lampblack exhibits a virtually neutral behavior, with a pH of 7.5.

Figure 23: Water-vapour adsorption isotherms of various pigment blacks

Table 7: pH values of pigment blacks

Pigment black type	pH
Gas blacks	4
Oxidized gas blacks	2 – 3
Furnace blacks	9 – 10
Oxidized furnace blacks	3 – 4
Lampblack	7.5

4.6.4 Volatiles at 105 °C

The loss of weight at 105 °C primarily reflect the moisture content of the pigment black. Moisture on the carbon black surface can have an influence on the application behavior. During the manufacture of plastic master batches, even small quantities of moisture have a negative effect, while in polar coating systems, a certain moisture content can have a positive effect on the wetting, jetness and hue.

Because of the manufacturing process, the pigment blacks are produced with only very low moisture contents, which are below 0.1%. However, during storage the pigment black takes up moisture from the surrounding air. Fine-particle, porous and in particular oxidatively after-treated pigment blacks (e.g. Colour Black FW 200) can pick up considerable quantities of moisture during storage, as can be seen from Figure 23.

4.6.5 Spectroscopic and spectrometric Methods for characterizing the Surface

Using secondary ion mass spectrometry (SIMS), it is also possible to derive statements about the state of hybridization of the C atoms from fragmentations and depth profiles. Using X-ray photoelectron spectrometry, it is possible to demonstrate that there are heteroatoms, such as O, N, S and metals, in the carbon black surface, and to determine their concentration and state of chemical bonding.

A very recent method is inelastic, incoherent neutron scattering (INS), which permits IR spectroscopy on the pigment black in the range from 18 to 4000 cm^{-1}. It is possible to distinguish between conjugated and isolated C-H structures and to make statements relating to the level of graphitization of the carbon black surface.

4.7 Purity

Pigment black may contain a series of impurities, which are introduced via the raw materials (carbon black feedstock, additives for setting the structure, quench water, conveying and combustion air), originate from the parts of the plant or are formed in the process itself. These impurities are coke, inorganic salts, catalyst residues from catcracker oils, dust, sand, rust, metallic or ceramic particles. In addition, on the carbon black surface it is also possible to find organic impurities whose nearly complete absence is necessary, in particular in the case of pigment blacks which are used for coloring items which come in contact with food.
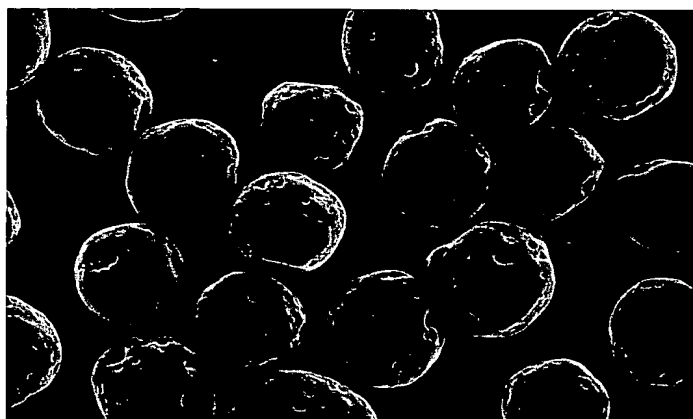
21

Figure 24: Typical particles of ball coke

Table 8: Methods for determining impurities

Method	Statement
Elemental analysis	Element composition
Ash content	Inorganic, non-volatile compounds in the form of their oxides, carbonates or sulfates, e.g. Ca and Mg salts from the quench and beading water, potassium salts from the setting of the structure, ceramic particles, sand, rust, catalyst residues from the raw material
Sieve residue	Water-insoluble, coarse-particle impurities, e.g. coke, ceramic particles, sand, catalyst residues from the raw material, rust, paper and fibers from the packaging
Toluene extract	Toluene-soluble, organic compounds
Electrical conductivity	Inorganic salts, acids

Coke is formed if the oily feedstock is not evaporated but converted directly into carbon. This occurs when the oil is poorly atomized (ball coke, Figure 24), or impinges on the hot reactor walls (refractory or impingement coke). Carbon black feedstocks having a high asphaltene content show a very high tendency to form coke.

Inorganic salts get into the pigment black via the quench water or the wet beading process, if deionized water is not used. A further source is the potassium salt which is used for setting the structure.

Because of the high gas velocities in the reactor, and the high mechanical stresses which are caused by this, ceramic particles can be detached from the reactor lining and get into the pigment black. Metals and rust originate from the parts of plant; dust and sand originate from the combustion or conveying air.

From the point of view of "purity", gas blacks and lampblack prove to be particularly advantageous. In both processes, the carbon black raw material is firstly evaporated, and only the oil vapor is transferred into pigment black, while the impurities which cannot be evaporated remain in the sump. In the lampblack process, the gas velocities are also very low, so that no erosion of the reactor lining is to be feared either. In any case, gas black apparatus consists of steel.

In spite of the large number of possible impurities, the actual quantities in pigment blacks are extremely small. In modern plant, raw and constructive materials and process control are optimized to reduce the content of those impurities. Residual foreign particles are virtually completely removed by gravity or centrifugal separators and powerful magnets.

4.7.1 Elemental Analysis

The main constituent of a pigment black, as expected, is carbon. In addition, it is possible to detect, to a small extent, the elements oxygen, hydrogen, nitrogen and sulfur, as well as traces of metals, such as calcium, magnesium and iron. Oxidized pigment blacks naturally exhibit an increased oxygen content, and in low-structure pigment blacks, larger quantities of potassium also occur. The proportion of heavy metals, which may be determined via a hydrochloric acid extraction or a determination of the ash content, is generally negligibly small (Technical Bulletin No. 25).

The contents of nitrogen and sulfur and of heavy metals depend causally on the raw material used. Sulfur is present in pigment black in elemental form and also in bound form as sulfane sulfur. Sulfates and sulfonates are also to be found in oxidized pigment blacks. As a rule, nitrogen is incorporated in the carbon lattice.

Table 9: Elemental analyses of pigment blacks

| Element | Furnace blacks | Ox. furnace blacks | Gas blacks | Oxidized gas blacks | Lampblack |
	% by weight	% by weight	% by weight	% by weight	% by weight
Carbon	97 – 99	96 – 98	94 – 97	80 – 90	98 – 98.5
Hydrogen	0.3 – 0.6	0.4 – 0.6	0.5 – 1.5	0.5 – 1.5	0.3 – 0.5
Oxygen	0.4 – 1.0	1.0 – 2.0	2.0 – 4.0	9 – 16	0.3 – 0.5
Nitrogen	0.2 – 0.3	0.2 – 0.3	0.1 – 0.2	0.5 – 1.0	0.4 – 0.6
Sulfur	0.1 – 1.0	0.1 – 1.0	0.3 – 0.6	0.3 – 0.6	0.3 – 0.6

4.7.2 Ash Content

The ash content permits conclusions to be drawn about the content of inorganic compounds in the pigment black since, at the predefined temperature of 675 °C, pigment black, coke and further carbon-containing material burns in air (Figure 25). The elements most frequently found in the residue are iron, calcium, magnesium, aluminum, silicon, sodium and potassium, which are present in the form of their oxides, carbonates or sulfates. Iron originates from the production plants, magnesium, calcium and sodium from the quench and beading water, aluminum and silicon originate from the ceramic reactor lining or from catalyst residues, and potassium originates

from the setting of the structure in the furnace black process. Iron is very easy to detect from the orange to red-brown color of its oxide.

The ash contents for Degussa-Hüls furnace blacks are <1%; in the case of gas blacks values of only 0.02% are found. Very low ash contents are required, for example, in the plastics sector.
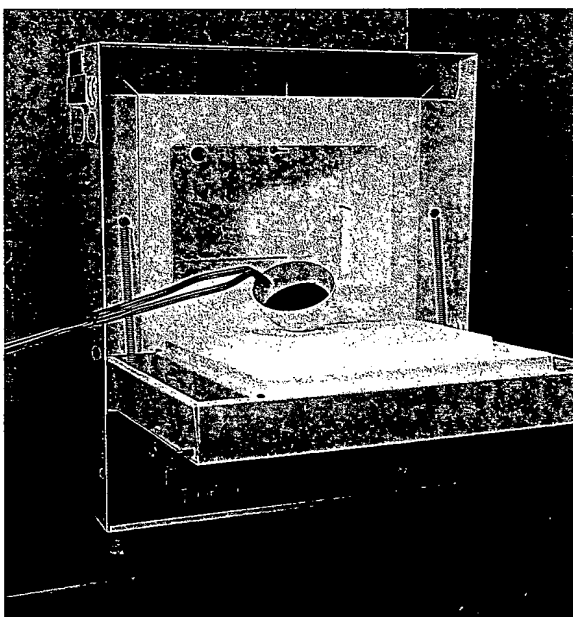
Figure 25: Determining the ash content in a muffle furnace
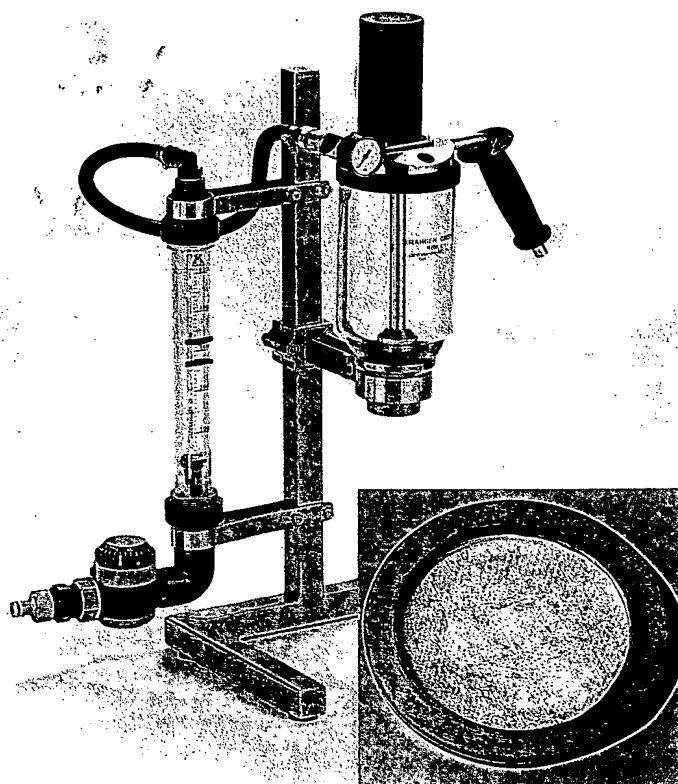
Figure 26: Mocker apparatus made of glass from Krahnen GmbH, Cologne, sieve insert with a mesh size of 44 μm.

4.7.3 Sieve Residue

The sieve residue provides information about the content of coarse particles, water-insoluble impurities, such as coke, ceramic constituents, metals and metal oxides, hard carbon black beads or highly compacted pigment black. In the determination according to Mocker, 50 g of pigment black are slurried in a little water and rinsed through a sieve with a mesh size of 44 µm or 25 µm using water at 4 bar (Figure 26). Water-soluble components are therefore not registered. The sieve residue is dried and determined gravimetrically.

In most cases, an optical microscope is sufficient to classify the different impurities using their color, shape and surface condition. Magnetic constituents may be detected with a bar magnet. If these means are not sufficient, the elemental composition of the individual particles on the surface may be determined, and hence their origin may be clarified, with the aid of X-ray microanalysis (RMA) or energy-dispersive X-ray microanalysis (EDX).

The sieve residue is of particular importance for extruded products and for spinning fibers.

4.7.4 Electrical Conductivity

In order to determine inorganic salts and acid residues in pigment black, the measurement of the specific electrical resistance or the specific electrical conductivity of aqueous pigment black extracts can be used. For this purpose, the pigment black specimen is extracted using deionized water. The electrical resistance or the electrical conductivity is determined in the filtrate.

4.7.5 Organic Impurities

Because of their manufacture, pigment blacks may still contain small quantities of polycyclic aromatic hydrocarbons (**PAH**). These **PAH**s are firmly adsorbed on to the carbon black surface and can be detached only under extreme conditions. In order to do this, the pigment blacks are extracted for 8 hours using boiling toluene (Figure 27). The toluene extract which remains after the solvent has been evaporated is considerably below 0.1% in the case of virtually all pigment blacks. The individual components of the toluene extract may be determined using gas chromatography.

In the rubber-carbon black sector, a statement of the toluene discoloration is common, being based on a cold extraction using toluene and the measurement of the light transmission at 425 nm. At high transmission values (= low contents of polycyclic aromatic hydrocarbons), this method differentiates too poorly and is, therefore, not suitable for answering questions relating to safety.

Figure 27: Soxhlet apparatus for determining the toluene extract

4.8 Physical Form and Handling Properties

Pigment blacks are available in powder and bead form (Figure 28). In the case of beaded carbon blacks, a distinction is in turn drawn between dry-beaded, wet-beaded and oil-beaded carbon blacks.

By comparison with powder grades, beaded pigment blacks have considerable advantages from an ecological, economic and application point of view:

- low dust levels,
- good flow behavior,
- well suited for silo storage and metering,
- high bulk density,
- low space requirement during storage and transport,
- reduced transport and storage costs,
- more rapid incorporation and wetting by binders (e.g. oil-beaded pigment blacks),
- lower viscosities after incorporation in a binder system or in plastic.

However, one significant disadvantage of beaded carbon blacks is that considerably more effort is needed for their dispersion, and the dispersion quality of a powder pigment black is not reached.

The selection of the correct product form - powder or beads - therefore also depends on the dispersion equipment available. Pigment blacks in powder form are to be recommended in the case of dispersion units having low shear forces (e.g. dissolvers and two-roll or three-roll mills). Beaded pigment blacks should only be used when dispersion units with high shear forces, such as pearl mills, ball mills or attritors, are available.

In the case of beaded pigment blacks, the bead hardness plays a decisive role. On the one hand, the bead hardness must be high enough for the granules not to be destroyed when they are being conveyed, transported or stored in silos, but, on the other hand, the bead hardness should be as low as possible, in order not to impair the dispersibility of the pigment black. In addition, the bead size distribution also has an influence on the dispersibility.

In order to characterize the beads, methods for determining the mass and individual pellet strength, the fines content and the pellet attrition are available.
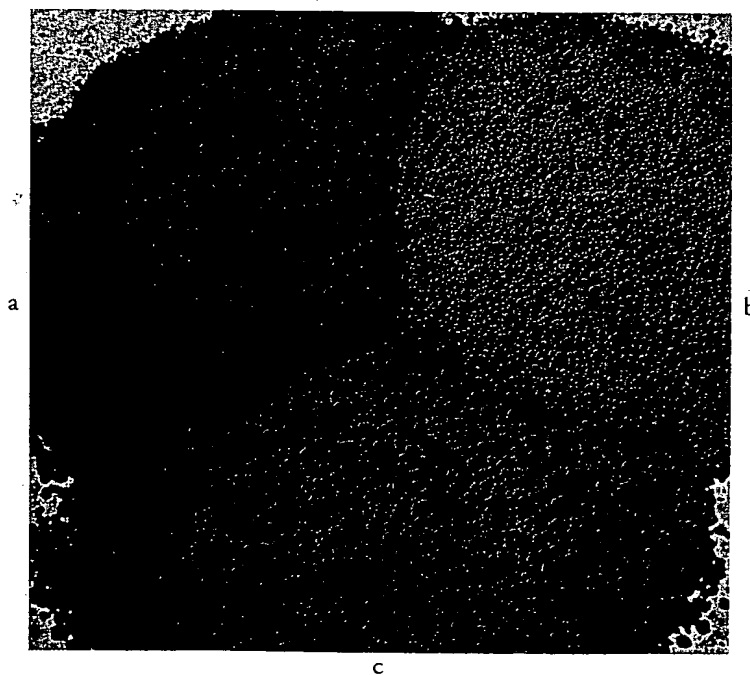
Figure 28: a) Powder pigment black, b) Dry-beaded pigment black, c) Wet-beaded pigment black

5. Coloristics

The first methods for characterizing pigment blacks were certainly coloristic measurements. They still have an important significance, since they certainly describe the two most important properties of the pigment black, namely the jetness and the tinting power of the pigment black. The carbon black color of the pigment black is therefore also part of the name in many languages.

The properties of the pigment blacks previously described, such as the primary particle size, structure, porosity and surface chemistry, permit predictions to be made about the coloristic appearance of the pigment blacks, but do not take into account their dispersibility, that is to say

- the mixing of the pigment black into the corresponding binder system,
- the expulsion of the air enclosed in the pigment black by the binder,
- the wetting of the pigment black surface by the binder,
- the mechanical breakdown of the pigment black agglomerates by milling,
- the stabilization of the milled particles by binders or wetting agents.

However, the performance of a pigment black depends to a very great extent on the degree of dispersion achieved and on the stability of this state in the respective system. It is therefore not possible to dispense with coloristic investigations. In the case of gas blacks, the determination of the jetness and of the tinting strength are the only methods which permit at least an indirect statement to be made about the primary particle size, if one disregards complicated electron microscopy.

5.1 Theoretical Consideration

If one considers the interaction between a carbon black particle having a diameter d and a light beam of wavelength λ, two effects have to be taken into account:

- the light scattering and
- the light absorption.

The light scattering can be explained by the wave nature of light. Internal fields are induced in the carbon black particle by a light beam and in turn lead to secondary fields being radiated. However, within the carbon black particle itself strong absorption occurs, that is to say a not inconsiderable proportion of the energy radiated in is converted into heat. Pigment blacks have a very high absorption capacity and a low scattering capacity, whereas in the case of white pigments the relationships are precisely the opposite.

The efficiency of scattering and absorption is determined by the ratio between the particle diameter d and the wavelength λ – the size parameter $\alpha = \pi \ast d / \lambda$ – and by the relative refractive index $m = n + i \ast k$ (n = real part, k = imaginary part). In the case of absorbing materials such as pigment black, $k > 0$, in the case of non-absorbing materials, $k = 0$. The refractive index of a pigment black exhibits a dependence on the C/H ratio.

Until now, the aggregates, consisting of grown primary particles, in the pigment black have been viewed as "particles" in the sense of light absorption and light scattering. However, more recent investigations have shown, that in the absorption and scattered-light measurements, the primary particles are weighted.

5.1.1 Light Absorption

For particles which are very small in comparison to the wavelength (Rayleigh range), that is to say for $d \ll \lambda$ and $\alpha \ll 1$, the **volume-related or mass-related** absorption is independent of the particle size, but inversely proportional to the wavelength of the light. If the wavelength and particle size are of the same order of magnitude (resonance region), the absorption is no longer independent of d but decreases with increasing particle size (at constant λ). For large particles (geometric optics), that is to say for $d \gg \lambda$ or $\alpha \gg 1$, the volume-related or mass-related absorption decreases with 1/d.

Table 10: Influence of wavelength and particle diameter on light absorption

Range	d/λ-ratio	Absorption
Rayleigh range	$d \ll \lambda$ or $\alpha \ll 1$	independent of d, $\sim 1/\lambda$
Resonance range	$d \approx \lambda$ or $\alpha \approx 1$	$\sim 1/d^n$ ($0 \leq n \leq 1$)
Mie range	$d \gg \lambda$ or $\alpha \gg 1$	$1/d$

This capacity to absorb light to a great extent imparts the carbon black color to the pigment black. The absorption itself takes place in the microcrystalline, graphitic region within the nanometer-sized primary particles. In the case of large particles, the effect of the "hidden mass" comes to bear, that is to say the radiation is absorbed in the outer layers and the mass at the centre no longer contributes to the absorption.

5.1.2 Light Scattering

For individual, homogeneous, spherical particles, the distribution of the scattered light can be described exactly in mathematical terms by the Mie theory. Rayleigh scattering represents a special case of the Mie theory for very small particles with $d << \lambda$ or $\alpha << 1$. In this size range, the **volume-related or mass-related** scattering intensity is proportional to the third power of the particle diameter and inversely proportional to the fourth power of the wavelength λ.

The result of this is that

- with increasing particle size, the intensity of scattering rises sharply. If the particle diameter is doubled, the volume-related or mass-related scattering intensity rises to 8 times its value
- with increasing wavelength of the light, the volume-related or mass-related scattering intensity decreases sharply. If the wavelength is doubled from 400 nm (= blue) to 800 nm (= red), the scattering intensity reduces to one 16th, that is to say light of a short wavelength is scattered significantly more sharply than light of a relatively long wavelength (blue sky and red sunset).

In the resonance range, that is to say when the wavelength and particle size are of the same order of magnitude, the scattering intensity reaches a maximum value. If the particle diameter is greater than the wavelength of the radiation, the volume-related or mass-related scattering intensity decreases with $1/d$.

Table 11: Influence of wavelength and particle diameter on the scattering of light

Range	d/λ-ratio	Scattering intensity
Rayleigh range	$d << \lambda$ or $\alpha << 1$	$\sim d^3$, $\sim 1/\lambda^4$
Resonance range	$d \approx \lambda$ or $\alpha \approx 1$	Maximum value
Mie range	$d >> \lambda$ or $\alpha >> 1$	$1/d$, $\sim 1/\lambda$

In the case of very small particles, no phase shifts occur in the scattered light, so that no destructive interference can occur. The scattering is isotropic, in other words the scattered light is propagated uniformly in all directions in space. In the case of larger particles, on the other hand, phase shifts occur in the scattered light and the scattered light is attenuated by destructive interference phenomena (superposition of phase-shifted scattered light beams). This leads to the scattered intensities being greater in the forward direction than in the rearward direction (Mie effect).

As the particles grow further, these differences becomes greater and greater.

5.1.3 Real Carbon Black Particles

The relationships indicated previously apply only to individual, homogeneous, spherical particles. For real carbon black particles, these preconditions are not satisfied, and the relationships are therefore extremely complex.

In real systems colored using pigment black, multiple scattering must be expected. The scattered light from a particle strikes a further particle and is in turn scattered there. Because of the high light absorption of pigment black, however, the intensity of the second scattered light already approaches zero. Multiple scattering therefore leads to an increase in the extinction coefficient and to a reduction in the scattered light.

Since the primary particles have grown into aggregates, the internal and external fields already have a mutual influence on each other within a pigment black aggregate. The aggregation leads to increased, volume-related scattering of the light, the aggregation probably leading to a very anisotropic radiation behavior. This effect is particularly clearly pronounced when the overall extent of the aggregate is of the order of magnitude of one half of the wavelength of the light. The aggregation effect is negligible in very small primary particles, because of the dominant absorption of pigment black in the Rayleigh range. The same is true of aggregates made of very large particles, since the scattering centers are far removed from one another and the condition of independently scattering particles is satisfied.

Further differences between theory and practice result from the deviation of the primary particles from the spherical shape and from the fact that the primary particles and aggregates are not of uniform size but have a size distribution (logarithmic normal distribution). In addition, in the case of inadequate dispersion, the remaining residues of agglomerates and their non-uniform distribution exert an influence on the optical properties.

These additional influencing variables are probably also the reason why the data available in the literature relating to the optical properties of pigment black, in particular to the refractive index, give a very non-uniform picture. The real part of the complex index of refraction is specified as lying between 1.4 and 1.7, the imaginary part between 0.3 and 0.7. For pigment black, refractive indices of $m = 1.7 + i*0.7$ or $m = 1.4 + I * 0.4$ are typically assumed.

5.2 Jetness

The jetness of a pigment black is understood to mean the intensity of the carbon blackening which can be achieved with it. The jetness of a material colored with pigment black is higher the lower the light reflection (= directly and diffusely reflected light). The achievable jetness depends on the particle size, the concentration of the particles in the dispersing medium and on the thickness of the absorbing layer.

As the primary particle size decreases, the jetness increases since – as described under 5.1.2 – the light scattering decreases considerably (Figure 29). It is therefore possible for the jetness to be used as an indirect measuring method for estimating the primary particle size. In linseed-oil varnish and other polar binders, oxidized gas black exhibits a somewhat higher jetness, because of better wettability.

In the case of fine-particle pigment blacks, an improvement in the jetness can be achieved by increasing the pigment black concentration; the multiple scattering benefits from the higher particle density, which leads to a reduction in the reflection. In the case of coarse-particle pigment blacks, on the other hand, the increase in light scattering predominates, so that the jetness decreases, even with an increasing pigment black concentration.

Figure 30: Influence of the structure on the jetness
(measured in accordance with DIN 55979)

According to the theory, the structure in fine-particle pigment blacks should have no influence on the jetness. Only from a particle size of >20 nm is an increase in the light scattering as a result of aggregation to be expected. In this primary particle size range, a high jetness is also achieved in fact in the case of furnace blacks by reducing the structure. The fact that the high-structure, fine-particle pigment blacks Printex 80 and Printex 90 even exhibit a higher jetness should be able to be attributed to inadequate dispersion of the low-structure, fine-particle pigment blacks (Figure 30).

5.2.1 Determining the Jetness

The most sensitive "instrument" for registering the often only very slight differences in the carbon black tones is the human eye. The practiced eye can distinguish up to 100 different black levels. For this purpose, a pigment black paste is prepared in a linseed-oil varnish and a visual comparison is carried out, in very bright parallel light (Leitz lamp), between this paste and a standard paste of known jetness. This method provides particularly good results when the sample paste is painted in between the pastes of a lighter and a darker pigment black.

Figure 29: Influence of the primary particle size on the jetness in gas blacks
(measured in accordance with DIN 55979)

Figure 31: Testing samples of coatings using a spectrophotometer

Figure 32: Testing samples of coatings with a densitometer

The low residual reflections from the pigment blacks can also be recorded by measurement using a spectrophotometer (Figure 31) or a densitometer (Figure 32). For this purpose, a pigment black paste likewise distributed in linseed oil is produced under standardized conditions. The jetness is specified as the blackness value M_y, which is calculated from the standard color value Y according to the following equation:

$$M_y = 100 * \log \frac{100}{Y}$$

If a densitometer is used, without a polarization filter, the M_y value is calculated from the visual density D_{vis} according to the following formula:

$$M_y = 100 * D_{vis}$$

A development of the paste methods previously described is the determination of the blackness value M_y in an alkyd/melamine-resin baking enamel. The advantage of this method is based on the fact that

- this test is very close to the customer in the coatings sector,
- in addition to the jetness, the hue can also be determined reliably,
- in addition to powder pigment blacks, beaded pigment blacks can also be used without further pretreatment,
- exactly defined synthetic raw materials are used,
- the prepared sample plates are "stable in storage".

High reproducibility is achieved by relating the M_y values to group standards. This results in relative carbon black values MYr. The absolute contribution of hue dM from the pigment black sample is obtained from the difference between the hue-dependent carbon black value M_c and the hue-independent carbon black value M_y (TI 1204).

5.3 Tinting Strength

The term "tinting strength" describes the capacity of a pigment black to darken another pigment. The addition of pigment black to colored pigments increases the light absorption and therefore the
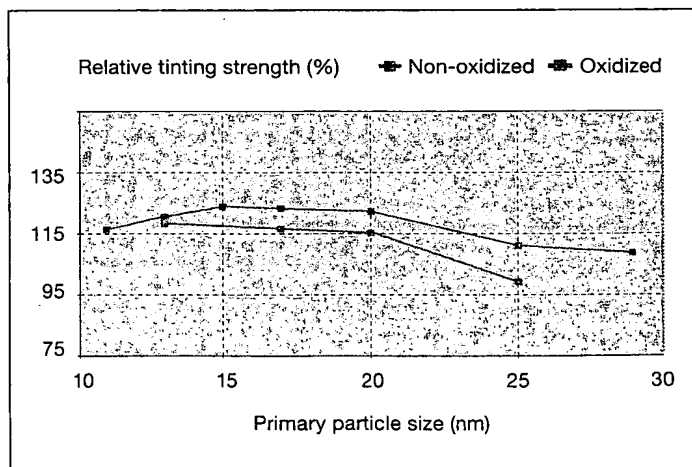
Figure 33: Influence of the primary particle size on the tinting strength in gas blacks (measured in accordance with DIN EN ISO 787-16/24)

Tinting strength in % DBP-number

95 52   100 48   114 52   123 105 66

140
120
100
80
60
40
20
0

Printex 90   Printex 80   Printex 40   Printex 9   Printex 30

14/15 nm   16 nm   26 nm   27 nm

Primary particle size
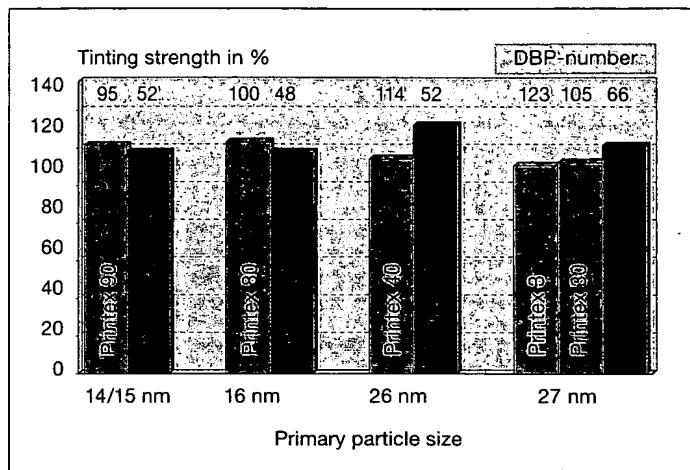
Figure 34: Influence of the structure on the tinting strength
(measured in accordance with DIN EN ISO 787-16/24)

brilliance of this system. Light scattered at colored pigment is absorbed more or less on its way to and from the carbon black particles.

In the same way as the jetness, the tinting strength of a pigment black also increases with decreasing primary particle size, since – as described under 5.1.2 – the light scattering decreases considerably. By contrast with the jetness, however, the tinting strength reaches an optimum at a primary particle size of about 20 nm. As the primary particle size decreases further, the value remains constant or even decreases slightly (Figure 33). This can be attributed to the fact that the dispersion conditions applied are not adequate to exhaust the available tinting strength reserve completely. The large discrepancy in the particle size between the fine-particle pigment black and the coarse-particle titanium dioxide used for the determination of the tinting strength makes optimum dispersion more difficult.

Oxidized pigment blacks exhibit a somewhat lower tinting strength, since absorbing carbon at the surface of the particle is replaced by non-absorbing, more strongly scattering oxygen. A broader particle size distribution likewise leads to a decrease in the tinting strength.

As in the case of the jetness, a clear increase in the tinting strength is achieved only beginning at a primary particle size of >20 nm, as a result of the reduction in the structure. In the case of fine-particle pigment blacks, hardly any differences can be detected (Figure 34).

Depending on the pigment black type and concentration, one achieves a light grey, dark grey, anthracite-colored or else a black coloration. If it is desired to adjust a color to be only slightly darker, then one speaks of shading with pigment black.

A high tinting strength is advantageous when the inherent color of a plastic (e.g. ABS polymer) or a plastic which is already colored (e.g. recycled plastic) has to be covered. Because of the high tinting strength, small quantities of pigment black are needed, so that the properties of the plastic are influenced as little as possible.

Only very low concentrations of pigment black are needed for shading. Use is therefore preferably made of pigment blacks having a low tinting strength, in order that discrepancies in the metering have a less severe effect. Suitable for this are lampblack (95 nm) and also relatively coarse-particle furnace blacks having particle sizes around 50 nm, which additionally offer the advantage of very easy dispersibility.

5.3.1 Determining the Tinting Strength

In order to determine the relative tinting strengths, firstly a pigment black paste in standard linseed oil is produced under standardized conditions (Figure 35) and is mixed in the ratio of 1:50 with a standard white pigment paste containing TiO_2. The white mixture obtained in this way is applied so as to cover a glass plate, and the tinting strength is assessed by a colorimeter. A relative tinting strength is specified, the tinting strength of the pigment black to be tested being referred to the tinting strength of the reference black IRB 3 (Industrial Reference Black), whose tinting strength is set equal to 100%.

White mixtures which have a lower tinting strength than the standard white mixture have relative tinting strength values <100%. White mixtures with higher tinting strengths than the standard white mixture have relative tinting strengths >100%.

Tinting strength and tint strength are not identical determinations. For the tint strength test method, zinc oxide is used as white pigment.
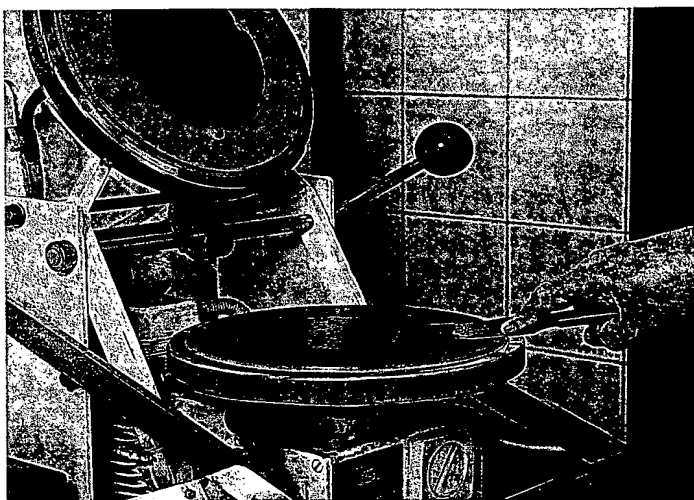
Figure 35: Grinding a pigment black paste using a mechanical muller

5.4 Hue

The different hue of pigment blacks is brought about by the fact that light absorption and light scattering depend on the wavelength of the light. Short-wave (= blue) light is scattered to a significantly greater extent than long-wave (= red) light; however, short-wave light is absorbed to a greater extent than long-wave light. A further factor which has to be taken into account is that, as the primary particle size increases, the intensity of the scattering and also the scattering in the forward direction increase sharply.

When visible light penetrates into a layer colored with pigment black in the "pure tone" (optically opaque), the short-wave blue components are scattered to a relatively greater extent than the long-wave red components, which penetrate into deeper layers. In the case of fine-particle pigment blacks, the scattering of the blue component takes place isotropically, that is to say the scattered light is propagated uniformly in all directions in space. Since a proportion is also scattered backwards, the carbon black coloration has a blue cast when viewed from above. In the case of coarse-particle pigment blacks, the scattering of the blue component in the forward direction dominates, whereas in the case of the red component, at the same

particle size, the forward scattering is less sharply pronounced. The result is that the coloration with a coarse-particle pigment black appears to have a brown cast when viewed from above.

When a layer colored with pigment black is viewed in transmission (that is to say in the case of a film which is not quite completely opaquely colored), the hue relationships are reversed. In the case of fine-particle pigment blacks, the layer appears to have a brown cast in transmission, since the red components are scattered and absorbed less. In the case of the coarse-particle pigment blacks, on the other hand, the result in transmission is a blue hue, since the short-wave, blue light is preferably scattered in the forward direction.

In "white mixtures" (grey tones), the relationships correspond to those when a pure tone coloration is viewed in transmission. In the case of fine-particle pigment blacks – as already outlined – the blue component is scattered diffusely. Only a small proportion of the scattered blue light strikes the white pigment and is scattered back, so that the "inherent color" of the white pigment dominates, and a grey with a yellow cast is produced at the surface. Coarse-particle pigment blacks, on the other hand, scatter the blue component preferentially in the forward direction, so that a considerable proportion of the blue light strikes the white pigment and is scattered back. The result for the observer is a gray with a less yellow cast or a greater blue cast.

In spite of these known relationships, the exact prediction of the hue is virtually impossible. The resultant hue of colorations using pigment blacks depends not only on the type of pigment black but also on the nature of the binder and of the wetting agents and additives used at the same time. In the case of white mixtures, the type of TiO_2 used also has a decisive influence. These effects ultimately have the level of dispersion achieved superimposed on them.

The hue can likewise be measured spectrophotometrically, and is given by the difference between the hue-dependent carbon black value M_c and the hue-independent carbon black value M_y.

6. Application Properties

As already mentioned, the primary particle size, surface area, structure, porosity and surface character are counted amongst the most important pigment black properties. Their influence on the application behavior is summarized in the following tables.

6.1 Influence of Primary Particle Size

	Primary particle size	
lighter	← jetness →	darker
browner	← undertone (masstone) →	bluer
weaker	← tinting strength →	stronger
bluer	← tinting undertone →	browner
lower	← binder demand →	higher
higher	← pigment loading →	lower
easier	← dispersibility →	harder
lower	← uv protection →	higher
lower	← electrical conductivity →	higher

6.2 Influence of the Structure

	Structure	
higher	← pour density →	lower
darker	← jetness →	lighter
bluer	← undertone (masstone) →	browner
stronger	← tinting strength →	weaker
browner	← tinting undertone →	bluer
lower	← binder demand →	higher
stronger	← pigment loading →	weaker
harder	← dispersibility →	easier
lower	← electrical conductivity →	higher

6.3 Influence of Porosity

Non-porous	Porosity	Porous
lower	← binder demand →	higher
higher	← pigment loading →	lower
harder	← dispersibility →	easier
lower	← electrical conductivity →	higher

6.4 Influence of the Surface Oxides

Non-oxidized	Surface oxides	Oxidized
lighter	← jetness →	darker
browner	← undertone (masstone) →	bluer
stronger	← tinting strength →	weaker
higher	← binder demand →	lower
lower	← pigment loading →	higher
harder	← wettability →	easier
harder	← dispersibility →	easier
lower	← gloss →	higher
higher	← electrical conductivity →	lower

Printex 45

Printex L

Printex 25

Printex 3

Special Black 5

Lamp Black 101

Printex 140

Printex 75

Printex 140 V

Printex 40

Special Black 4

Special Black 350

Printex alpha

colour Black
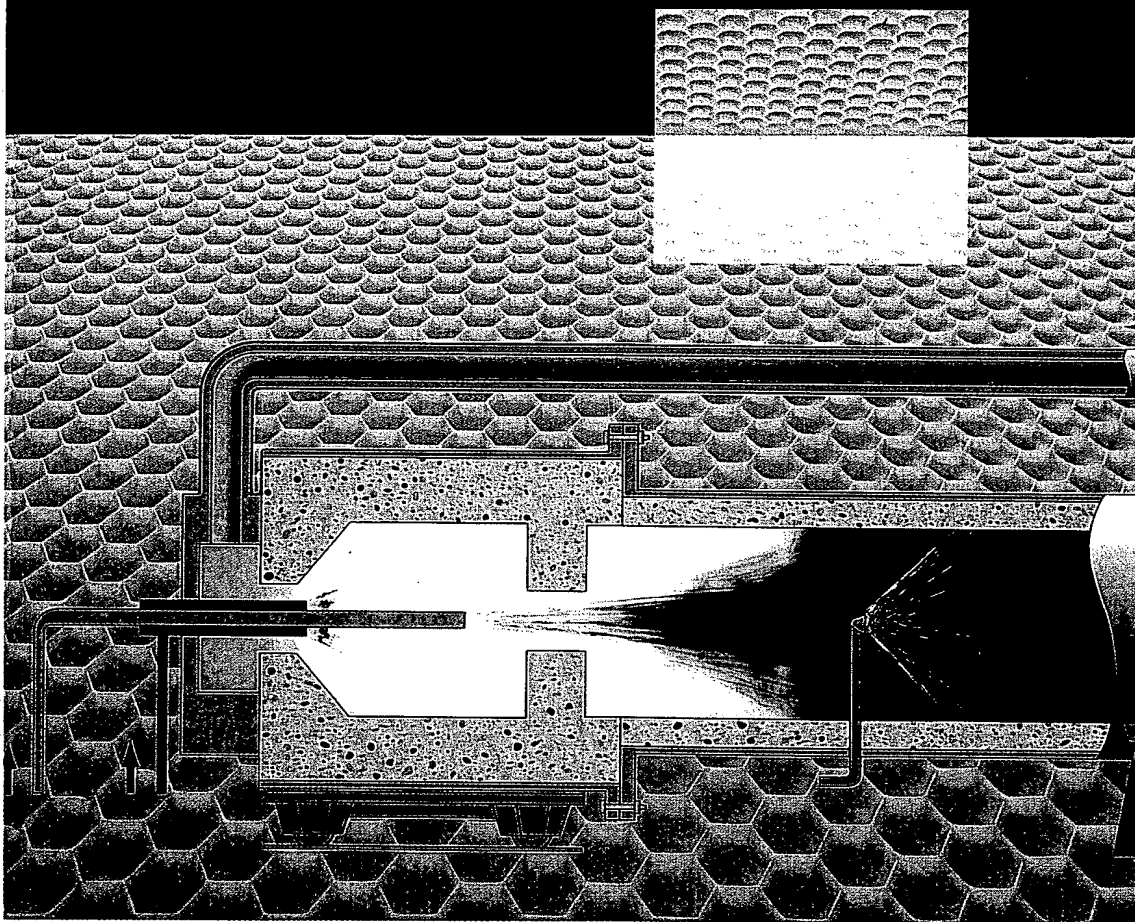
What is Carbon Black?

What is Carbon Black?

...not just a scientific name for soot.

Contents

Fig. 1:
Candlelight: a prototypical carbon black
production process. Only, soot would be the
more appropriate term here.

To answer the question:
What is Carbon Black? does not seem
to be particularly difficult, and almost every-
body believes to know the answer. This is
because in our daily lives we frequently encounter
emissions of a similar coloured substance, namely
"soot", from various sources such as billowing chim-
neys, exhaust particles from diesel-engines, malfunc-
tionaly oil fired heating systems or smoke from burning
fields and meadows in autumn.

One way of making the distinction between defined industrially produced carbon black and undefined created black would be to say that soot just happens – in other words, it's production is an unintentional by-product of some form of combustion process and it's not reclaimed after it is emitted. Carbon black, on the other hand, is the result of processes specifically designed with the product of "soot" in mind. Where soot is used as a general term for an undefined substance, the designation "carbon black", a term also accepted in many non English-speaking markets, implies a purpose and a technical process to produce it.

In this brochure we will explore the various methods for producing carbon black. These are processes that can be precisely defined and controlled, resulting in specific, repro-ducible and consistent carbon black quali-ties for the most diverse applications. There are more than 100 individual grades (note: in this case type implies a production process) of carbon black on the market today, each with its own distinctive set of characteristics and properties that make it suitable for a very narrowly defined purpose. By contrast, the soot that comes as a by-product of combustion processes does not occur under such precisely engineered conditions. It therefore contains various impurities that make it easily distinguishable from carbon black, if not in terms of colour, certainly in terms of quality.

This brochure proposes to explore the world of carbon black and its possibilities in modern industrial applications.

The semantics of soot		
	Undefined	Defined
English	Soot	Carbon Black
German	Ruß	Industrieruß
French	Suie	Noir de Carbone
Italian	Fuliggine	Nero di Carbonio
Spanish	Hollin	Negro de Humo

Table 1:
The semantics of soot – how the distinction is made in other languages.

The broad spectrum of applications (Table 2) results in a variety of carbon blacks where each type is designed to meet specific requirements. So called **rubber blacks**, for instance, used to reinforce rubber in tire and mechanical rubber goods, fulfill different prerequisites as **pigment blacks** used in printing inks and coatings or, in some cases, to provide UV protection of polyolefines. At the same time, carbon blacks can be used to modify the conductivity or antistatic properties of polymers which are involved in both rubber and non-rubber applications **(conductive carbon blacks).**

Understandably, users of carbon blacks place high demands in terms of specification and consistency of quality. Here, the various **manufacturing processes** and **raw materials** involved in carbon black production not only meet these specific requirements, but also make it possible to develop carbon blacks with a specific profile of properties.

Though individual grades may vary, more than 98% of the world's annual carbon black production is achieved with the **furnace black process**, representing more than 7 million metric tons. Processes other than furnace are also involved in the commercial manufacture of carbon black, these include the processes for the production of **gas blacks, lamp blacks, thermal blacks and acetylene blacks.**

The variety of carbon blacks, production methods and areas of application show that "soot" has come a long way. Of course, much has been published about the subject in technical journals, textbooks, reference works and product brochures. What we propose to do is to distill the important facts and show the many interesting facets of a product that is so simple and at the same time so sophisticated. Indeed, many of the things we take for granted in our everyday lives would not be possible without carbon black.

History of Carbon Black
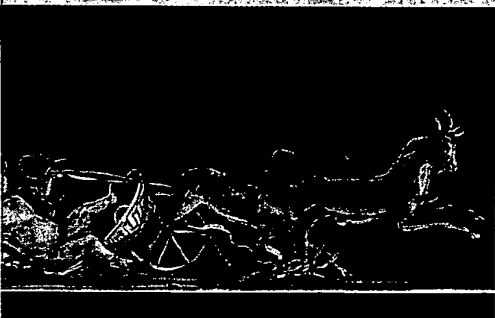
Fig. 16:
Roman fresco, Pompeii

Ancient civilizations in China and Egypt mixed soot into resins, vegetable oils or tar to create colors and inks. By allowing a flame, usually from an oil lamp, to come in contact with a cooled surface the soot accumulating on that surface could then be scraped off and collected as a powder. This process, referred to as the impingement process, using the flame from an oil lamp was a percursor to today's lamp black process however it is also the basis of the channel and gas black processes which utilises gas flames impinging on cool cast iron channels or rotating cooled cylinders.

Later on, the Greeks and Romans had a predilection for black to decorate walls, resulting in a great need for soot (Fig. 16). In what has become a standard work of antiquity, "De Architectura," Roman master builder Vitruvius describes in painstaking detail a technical method in which resin is fired in a brick-lined furnace and carbon black is precipitated in large quantities in a special chamber (Fig. 17).

a)

4

Major carbon black applications	
Area	Application
Rubber	Reinforcing filler in tires and mechanical rubber components
Printing inks	Pigmentation, rheology
Coatings	Black and grey pigmentation, tinting
Plastics	Black and grey pigmentation, tinting, UV protection, conductivity, conductor coating
Fibers	Pigmentation
Paper	Black and grey pigmentation, conductivity, decorative and photo-protective papers
Construction	Cement and concrete pigmentation, conductivity
Power	Carbon brushes, electrodes, battery cells
Metal reduction compounds	Metal smelting, friction compound
Metal carbide	Reduction compound, carbon source
Fireproofing	Reduction of mineral porosity
Insulation	Graphite furnaces, polystyrene and PU foam

Table 2:
Major carbon black applications

Fig. 17:
Description of carbon black production process in "De Architectura" by Vitruvius
a) Medieval manuscript
b) Latin text
c) English translation

Marcus Vitruvius Pollio
Ten Books on Architecture (Volume VII, Chapter 10)
Black Pigments

Now I come to the pigments, which are converted in such a way that they take on the characteristics of color pigments only when mixed correctly with other materials and when certain (chemical) processes are employed. First, I want to present the black pigment, the use of which is indispensable in construction. The techniques required to produce the correct mixtures must be known so that these mixtures can be prepared by skilled workers under appropriate conditions.

First, a vaulted chamber is built in the form of a (Roman) steam bath, lined carefully on the inside with marble stucco, and smooth. In front of this chamber a small combustion chamber, and with the inlet opening closed exactly far enough so that the flame does not shoot out.

Pine resin is now placed in the furnace. During burning, carbon black develops from the resin because of the great heat: this carbon black passes through the outlet openings into the separation chamber, and is precipitated on the rounded sections of the chamber and of the vaulted ceiling. The carbon black is then collected, with the largest amount of it incorporated into gum Arabic in order to produce black ink. The remainder is mixed with glue by stucco workers, and is used as wall coating.

However, when there is no supply on hand, another procedure must be employed. If the work is not to be postponed due to the delay that must be expected. In such a case, pine brushwood and pine chips must be fed into the fire; when the brushwood and chips have been converted to charcoal and extinguished, they can be ground with glue in the mortar. In this way, a black color is derived which is highly esteemed by stucco workers.

In addition, a black coloring agent is produced from wine yeast when this yeast is dried, heated in the furnace, and when the charcoal developed is then ground with glue; when applied to the wall, this coloring agent results in an unsurpassed, pleasant coloration. Finally, when yeast from finer types of wine is used, it is not only possible to produce a black pigment, but also the blue color of the indigo can even be imitated.

b)

c)
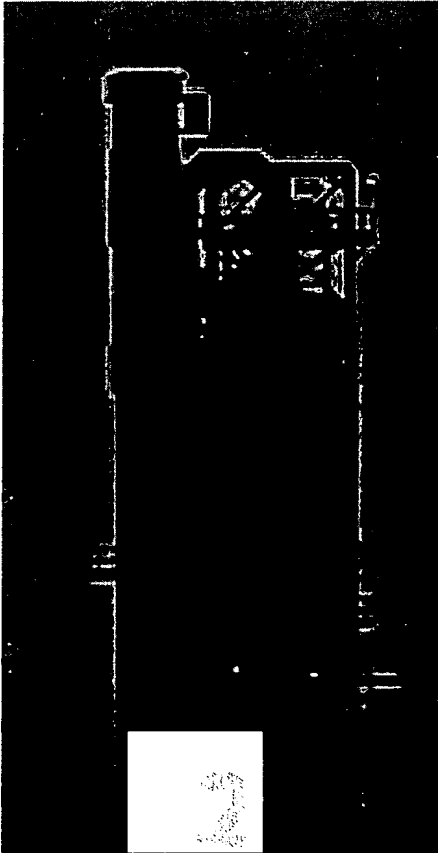
In answer to the question "What is carbon black?" the impact of the production method on the properties of the end product suggests that we should first focus on the methods available before describing these various properties. That is because they are defined at the earliest stage of the manufacturing process, regardless of whether it's a carbon black for use in the rubber and plastics industry, the printing industry or for conductivity applications.

History of Carbon Black

The process has essentially remained the same since Vitruvius first described it. Centuries later, the invention of the letter press would create an even greater demand for carbon black, as writing inks, having water-like consistancies, had to be replaced with more viscous printing inks (Fig. 18). As a result, manufacturing carbon black became a trade, with many entrepreneurs setting up shops with a furnace to produce lampblack. Fig. 19 shows a furnace such as those in use during the 18th century.

Pine resin proved an ideal raw material for carbon black used in printer's inks, and Germany's Black Forest region soon became the epicenter of a thriving industry. Special settling chambers made it possible to conveniently produce large quantities of carbon black (Fig. 20).

Fig. 18.
Excerpt from CORNUPIAE, a Latin-German dictionary published in 1780.

The basic **raw material** for producing carbon black consists of **hydrocarbons** that are split into their constituent elements, carbon and hydrogen, by either a **thermal** or **thermal-oxidative (partial combustion)** process. Economically, the thermal-oxidative decomposition has become the predominant method, with the hydrocarbons taking on a double role since they serve both as a source of heat and of carbon.

A burning candle easily demonstrates how it works. The outermost zone of the flame is where some of the hydrocarbons can burn as there is ample supply of oxygen nearby to feed the combustion process. This in turn generates the heat required to melt and vaporize the wax, the dark area surrounding the burning wick is in fact wax being transformed into vapor. In the inner, luminous zone, there is a defficiency of oxygen and it is in this region that the soot forms, visible as the thin black trail that floats up from the tip of the flame.

It can be collected by bringing the reacting gases into contact with a cooled surface.

Every carbon black production method is based on the two fundamental elements of heat and decomposition; how these stages are arranged is what defines the difference between the production processes.

Production methods/Raw materials

Chemical process	Manufacturing method	Main raw materials
Thermal-oxidative decomposition	Furnace black process	Aromatic oils on coal tar basis or mineral oil, natural gas
	Degussa gas black process	Coal tar distillates
	Lampblack process	Aromatic oils on coal tar basis or mineral oil
Thermal decomposition	Thermal black process	Natural gas (or mineral oils)
	Acetylene black process	Acetylene

Table 3:
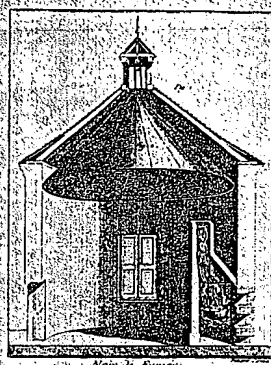*Production methods*
and raw materials
for carbon black.

Fig. 19:
Ancient lampblack process as described in Diderot's "Encyclopédie" (Paris 1770/80)
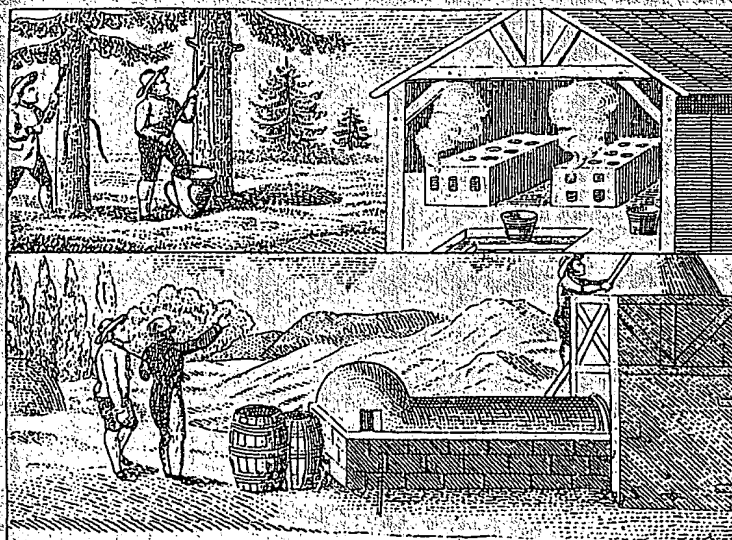
Fig. 20:
Processing pine resin to create pitch, tar and carbon black.

Harz=, Pech=, Theer= und Kienrußbereitung.

2.1 Raw Materials

The preferred feedstock for most carbon black production processes, especially the furnace process, are heavy oils which are composed mainly of aromatic hydrocarbons. The aromatic form of carbon gives the greatest carbon to hydrogen ratio, thus maximising the available carbon, and is the most efficient in terms of carbon black yields. In theory the greater the aromaticity the more efficient is the process. Unfortunately as the number of combined rings increases, the substances move from viscous liquids to solid pitches. Therefore in reality the most suitable oils are those in which the majority of the carbon is in the form of substances comprising three or four-membered rings.

Distillates from coal tar (carbochemical oils), or residual oils that are created by catalytic cracking of mineral oil fractions, and oleofine manufacture by the thermal cracking of naphta or gasoil (petrochemical oil), also qualify as a source of raw material.

Quality is the main criteria for deciding in favor of a specific feedstock. Here a variety of properties are important: Density, distillate residue, viscosity, carbon/ hydrogen ratio, asphaltene content, specified impurities, etc. All come into play in the desired feedstock specifications. The BMCI (Bureau of Mines Correlation Index) provides a measure of aromaticity based on either density and average boiling point or viscosity and API gravity. Economically a suitable feedstock should have an index above 120.

However, the BMCI is really only applicable to feedstocks derived from petroleum. In the case of carbochemical oils the BMCI may not reflect the true aromaticity of the product. For this reason the carbon/hydrogen ratio is more favoured for carbochemical products. However, as this measurement is also superior to BMCI even for petrochemical products, the carbon/hydrogen ratio or the carbon content are becoming the preferred criteria for all carbon black feedstocks.
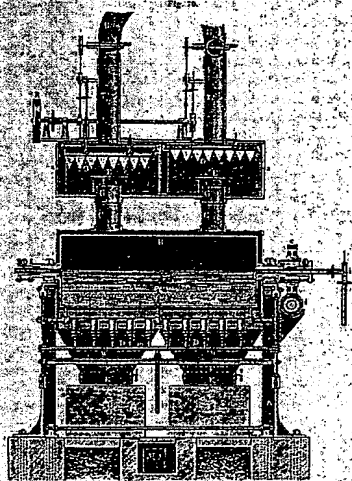
History of Carbon Black

The industrial revolution eventually also took carbon black production to higher volumes by making coal tar available in large quantities. The lampblack process was also perfected to include a labyrinth collection chamber. Even though yield was substantially increased, the carbon black was only incompletely precipitated.

Lampblack chambers based on this design continued in operation until the middle of the 19th century before they gradually were replaced by more environment-friendly filter systems.

Towards the end of the 19th century, the carbon black industry on the other side of the Atlantic had developed a process with natural gas as feedstock. The main reason

was the ample supply of this inexpensive resource, and the realization that the firing process produced a special type of carbon black. The firing plants were designed in such a way that they could easily be moved to another site once a well was depleted. This so-called channel black quickly experienced growing demand when its reinforcing properties became clear to the rubber industry, properties which lampblack did not offer. The finer particles of the channel blacks made it possible to increase tire longevity to several tens of thousands of miles. In retrospect, the automobile industry owes much of its rapid growth to the discovery and refinement of channel black production.

In Europe, the scarcity of natural gas led to the development of an analogous method based on coal tars. By 1935, Degussa's gas black system (Fig. 21) proved a viable alternative to the American channel black

Fig. 2.1: Gas black manufacturing apparatus as depicted in German patent application DRP 29261.

2.2 Thermal-Oxidative Process

Additional quality requirements involve impurities from foreign matter. Alkaline metals, for instance, are important because they have a direct affect on a specific carbon black property. The sulfur content of the oil can also play a significant role in production operations since in many countries producing sites have to meet rigorous environmental standards. Sulfur emissions from combustion processes are restricted by law. Furthermore carbon blacks having high sulfur contents might be prohibitive for certain applications. As we look into the various production methods we will also address the different raw materials that can be used to produce carbon black.

2.2.1 Furnace Black Process

Historically the most recent process, the furnace black method (Fig. 2), has also become the most common in large scale carbon black manufacturing. The furnace black method is continuous and uses liquid and gaseous hydrocarbons as feedstock and as a
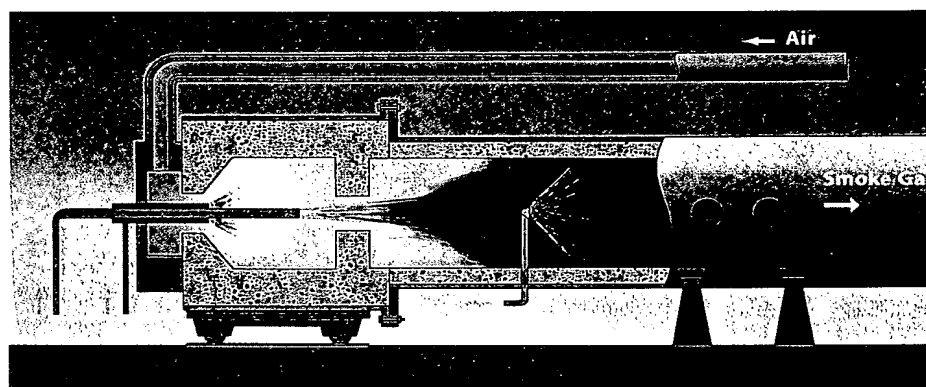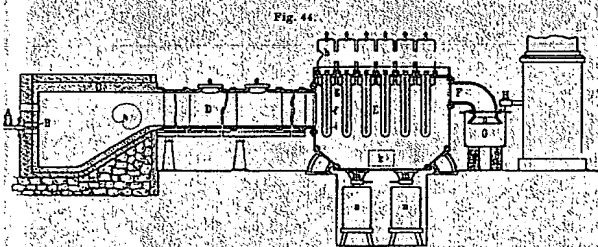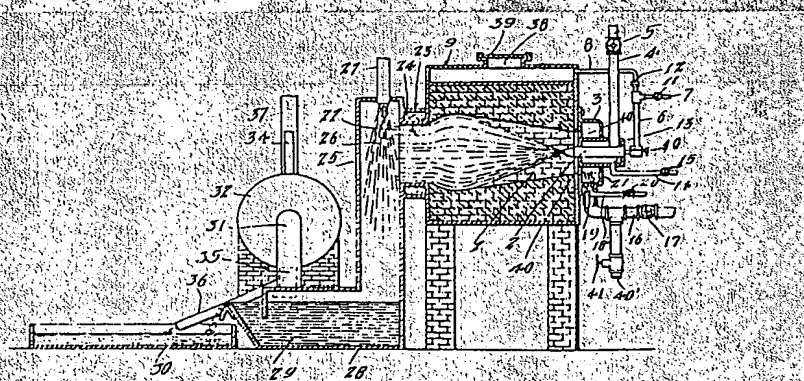

Fig. 2:
Scheme of a furnace black reactor.

Fig. 22:
a) Furnace black reactor, German patent DRP 50605 of 1899.
b) Furnace black reactor, US patent 1,438,032 of 1922.

method. Until after WWII the whole tire industry was dominated by the channel black method in the US and the gas black method in Germany.
As early as the 19th century (Fig. 22 a, b), and then more intensively in the 1920s, attempts were made to produce carbon black in a completely closed system with mineral oil as feedstock. Though the gas furnace process played a certain role in the US, the oil furnace method first commer-

cialised in 1943 eventually became the method of choice. Today, 98% of the world's carbon black is produced according to this process.

heat source respectively. When natural gas is available, the liquid feedstock is sprayed into a heat source generated by the combustion of the natural gas and pre-heated air. Because it occurs at a very high temperature, the reaction is confined to a refractory-lined furnace, hence the name (Fig. 3). After the carbon black is formed, the process mixture is quenched by the injection of water. This also prevents any unwanted secondary reactions. The carbon black ladened gas then passes through a heat exchanger for further cooling, whilst simultaneously heating up the required process air. A bag filter system separates the carbon black particles from the gas stream. The gases produced by the reaction are combustible and in most cases are fed into an afterburning stage where the heat is used to dry the carbon black or burnt in a boiler to generate steam. The carbon black collected by the filter has a very low bulk density and, depending on the application, is usually pelletized or further densified to facilitate onward handling.

The wet-pelletizing process uses water and a binding agent in a specially designed wet pellet or "pin" mixer which transforms the carbon black into spherical pellets which are then dehydrated in rotary dryers. The binding agent ensures that the product is resistant to attrition as well as easy to process and transport.
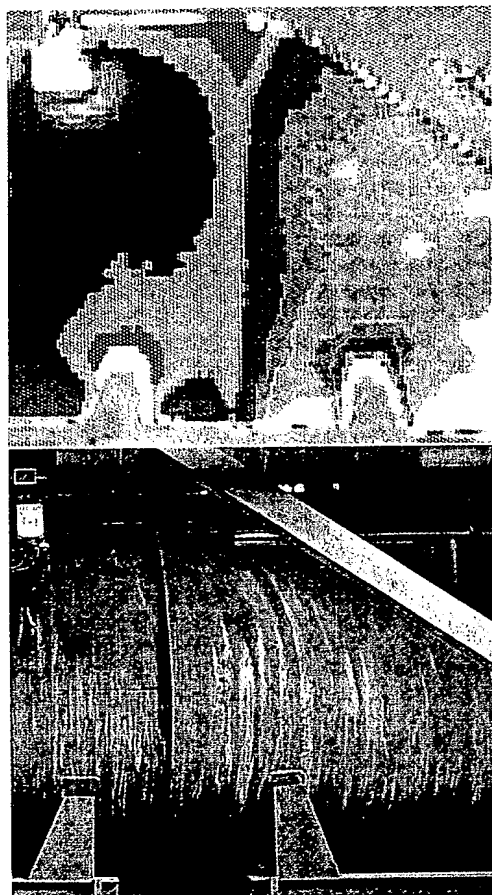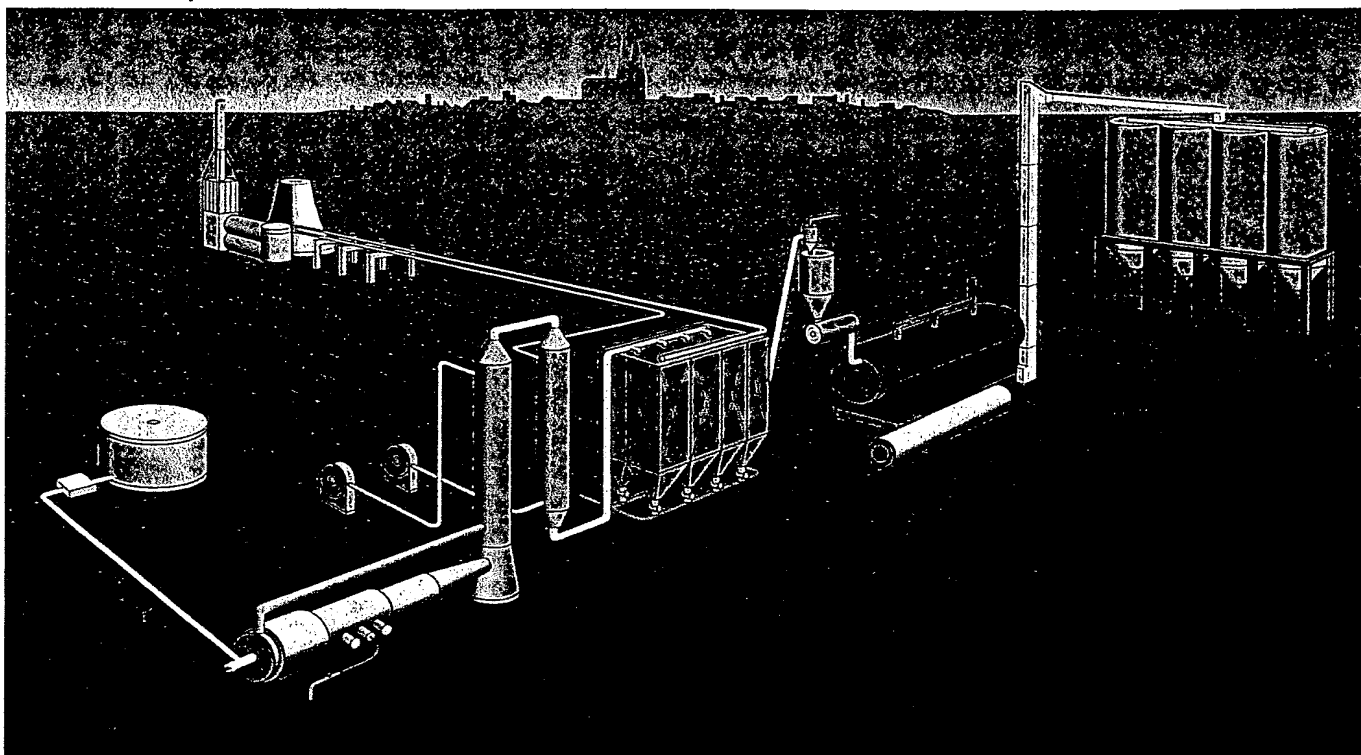

Fig. 3:
Furnace black reactor (section)
1) Heat imaging using an infrared scanner.
2) Daylight photograph.

The incorporation of these pellets into a polymer matrix requires subtantial shear forces, mostly applied by internal mixers in the rubber industry.

Pigment blacks produced by the furnace black process are loosley densified and packaged as powder blacks or are transformed into easily dispersible pellets by application of the dry-pelletizing process (Fig. 5).

Oil-pelletized blacks, used primarily in the pigment industry, are an additional variant utilizing mineral oils in the pelletization process. Because of the light oil coating, these carbon blacks are characterized by even easier dispersion and virtually dust-free handling.

The furnace black method offers environmental and work safety benefits, the fully closed installation keeps the emission of process gases as well as dust to a minimum (Fig. 6).

Besides its environmental, economic and technical advantages, it also allows for a greater flexibility in that it is capable of manufacturing more different grades of carbon black than any other process currently used. All raw materials are precisely specified in terms of quality, type and quantity. This makes it possible to produce a broad range of carbon blacks which are suitable for use in various applications without fundamentally changing the process for

Fig. 4:
Furnace black production installation

Carbon black created from gas and oil in a reactor with pre-heated combustion air is passed through a filtering stage and separated from other emissions. The product is then wet-pelletized, dried in a rotary drier and then fed into a storage silo. The gaseous emissions and heat resulting from the process are used to generate steam in a boiler.

each product variant. For instance, particle size or specific surface area can easily be defined at the outset by setting the appropriate process parameters. The furnace process also permits the manufacturer to control particle aggregation, the so-called carbon black structure, by adding small quantities of an alkaline metal salt.

In terms of particle size, the furnace black can be produced by having primary particles in the range of 10 to 80 nanometers. It takes an electron microscope to define the actual particle sizes and structures (Fig. 7).

To this day, however, it has not been possible to replicate the unique properties of gas and lampblacks with the furnace black method.
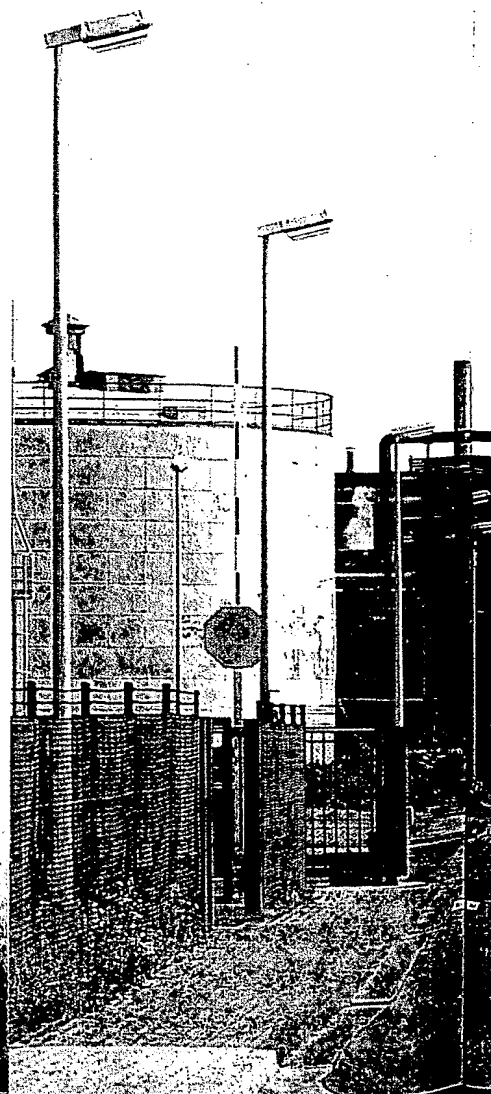

Fig. 5:
1) Powder carbon black
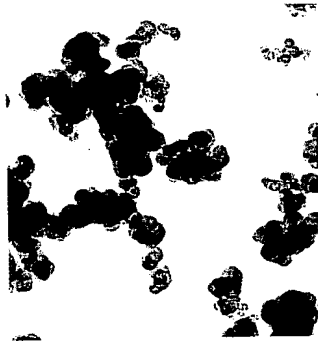*2) Dry-pelletized carbon black*
3) Wet-pelletized carbon black

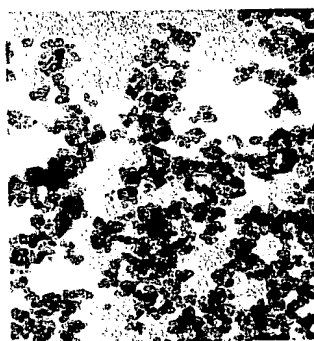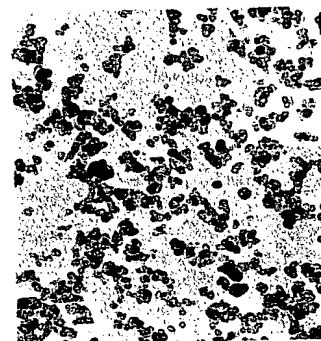

Fig. 6:
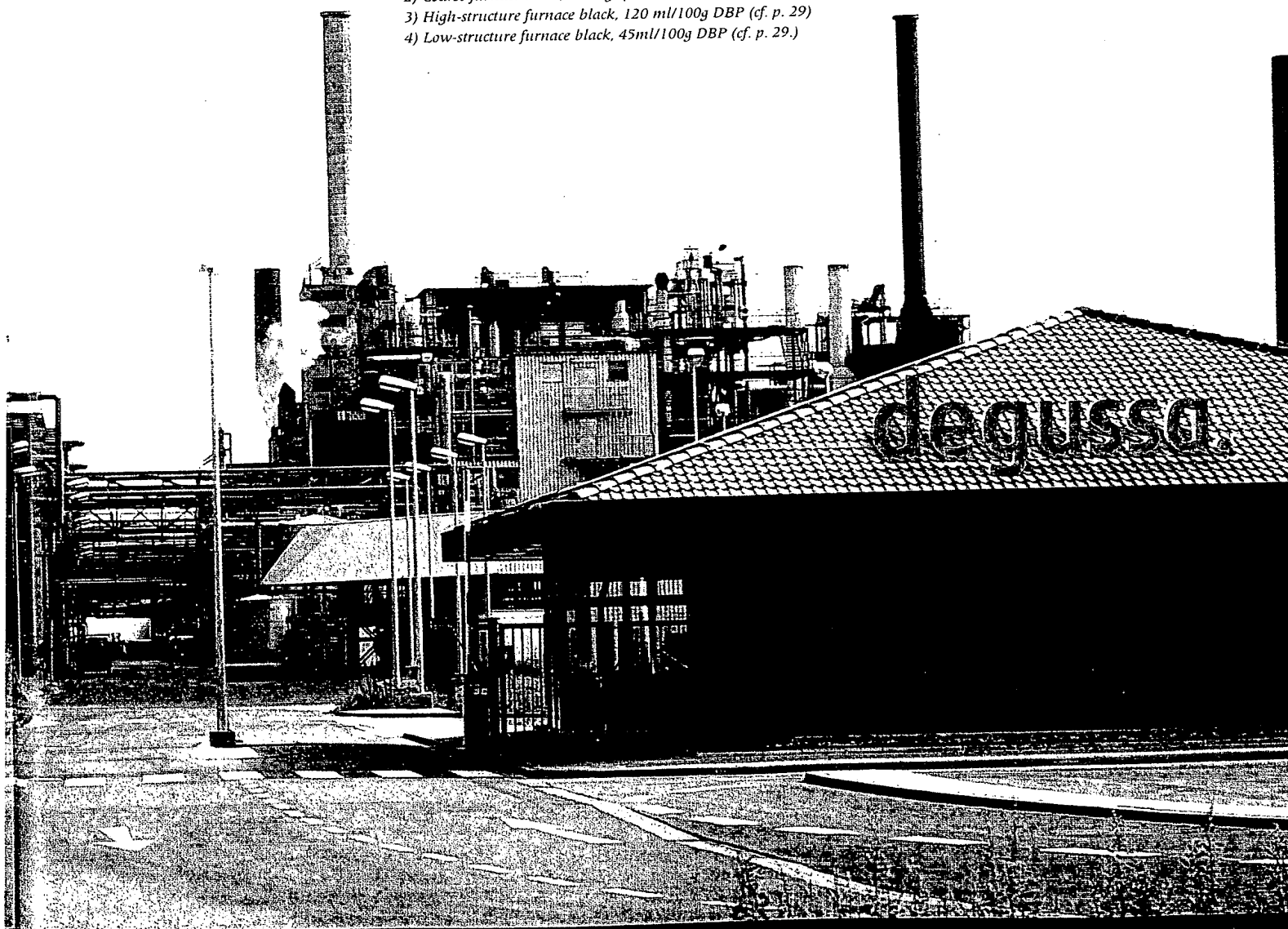*Degussa carbon black plant in*
Kalscheuren nearby Cologne.

Fig. 7:
Furnace blacks of varying particle size and structure
1) Fine furnace black, average particle size: approx. 14 nm
2) Coarse furnace black, average particle size: approx. 50 nm
3) High-structure furnace black, 120 ml/100g DBP (cf. p. 29)
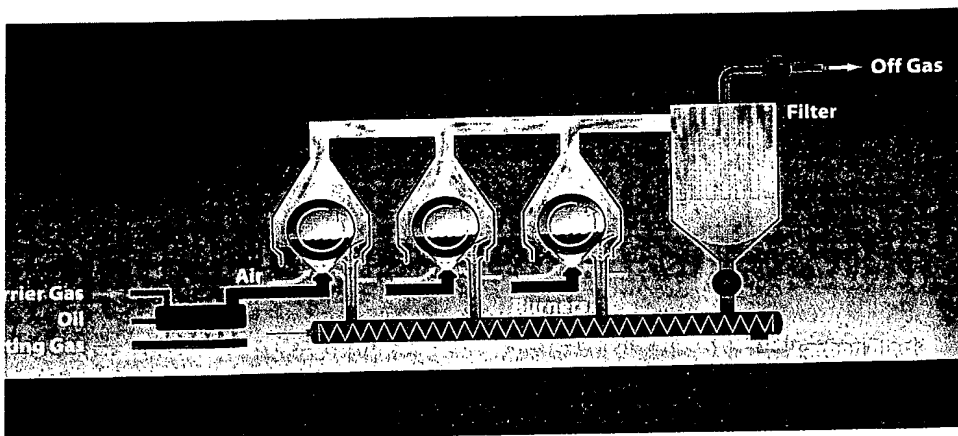4) Low-structure furnace black, 45ml/100g DBP (cf. p. 29.)

Fig. 9: Electron microscope view
of gas black particles (FW 1.)

Fig. 8:
Scheme of gas black production plant.

2.2.2 Degussa Gas Black Process

The gas black method developed by Degussa, in the mid-thirties is closely related to the channel black process developed in the US, based on natural gas as feedstock. As this resource was much scarcer in Europe, the Degussa gas black method was developed to use coal tar distillates as raw material instead.

In contrast to the channel black process, which pose a substantial burden on the environment, gas black plants are at the cutting edge of environmental technology. The facilities are constantly vacuum cleaned and the carbon black is collected in sealed filter systems that exceed official emission standards by a significant margin.

As feedstock the gas black process uses oils instead of natural gas. The oil is heated in a vaporizer and the resultant vapours are carried by a hydrogen rich gas into a gas tube fitted with a multiplicity of burners, and the individual flames so produced impinge on the surface of a water-cooled drum (Fig. 8). A portion of the carbon black generated is deposited on the roller while the rest enters the filter system. In the next stage the two carbon black streams are combined. Onward processing is then similar to the furnace black process.

While it is possible to control the raw material fed by the carrier gas stream, the air has free access but despite this restriction, the gas black method allows particle sizes within a range of 10 to 30 nm to be produced. The trade off is less flexibility in defining the structure. This, however, is not necessarily a disadvantage as gas blacks are inherently characterized by a loose structure and exceptional dispersibility.

While in the past these types of carbon black were used predominantly in tire tread formulations, they are now used almost exclusively in pigment applications where the fine-particle gas blacks are of particular importance (Fig. 9).

As a result of contact with oxygen at high temperatures, acidic oxides form on the surface of the carbon black particles. In contrast to furnace blacks, gas blacks thus display an acidic reaction when suspended in water.

Oxidative post-treatment using NO_2, ozone or other oxidants also make it possible to further increase acidic surface groups significantly. These treated carbon blacks are also used mostly in the pigment sector, e.g. in the coating and ink industries. In view of the volume demand, most gas blacks are treated oxidatively.

2.2.3 Lampblack Process

The lampblack process is the oldest commercial carbon black production process.

However, besides the general principle, today's lamp black production units have very little in common with the ancient carbon black ovens. Smoking chimneys and settlement chambers have long since given way to highly sophisticated filtering systems.

The lampblack apparatus consists of a cast-iron pan, that holds the liquid feedstock, which is surmounted by a fire-proof flue hood lined with refractory bricks. The air gap between the pan and the hood, as well as the vacuum present in the system, help regulate the air supply and thus enable the manufacturer to fine tune the carbon black's ultimate properties. Though radiant heat from the hood causes the raw material to vaporize

and partially combust, most of it is converted into carbon black (Fig. 10).

In order to separate the solids, process gases containing carbon black are passed through a filter after the cooling stage. Onward processing is similar to that of the furnace black method as described in section 2.2.1.

Although in the past, different types of lampblacks were produced, the method was eventually standardized to yield only one type of pigment black and one type of rubber black. These carbon blacks are characterized by a broad primary particle size distribution, ranging from approximately 60 to over 200 nm (Fig. 11) and are widely used in a number of specialised applications.
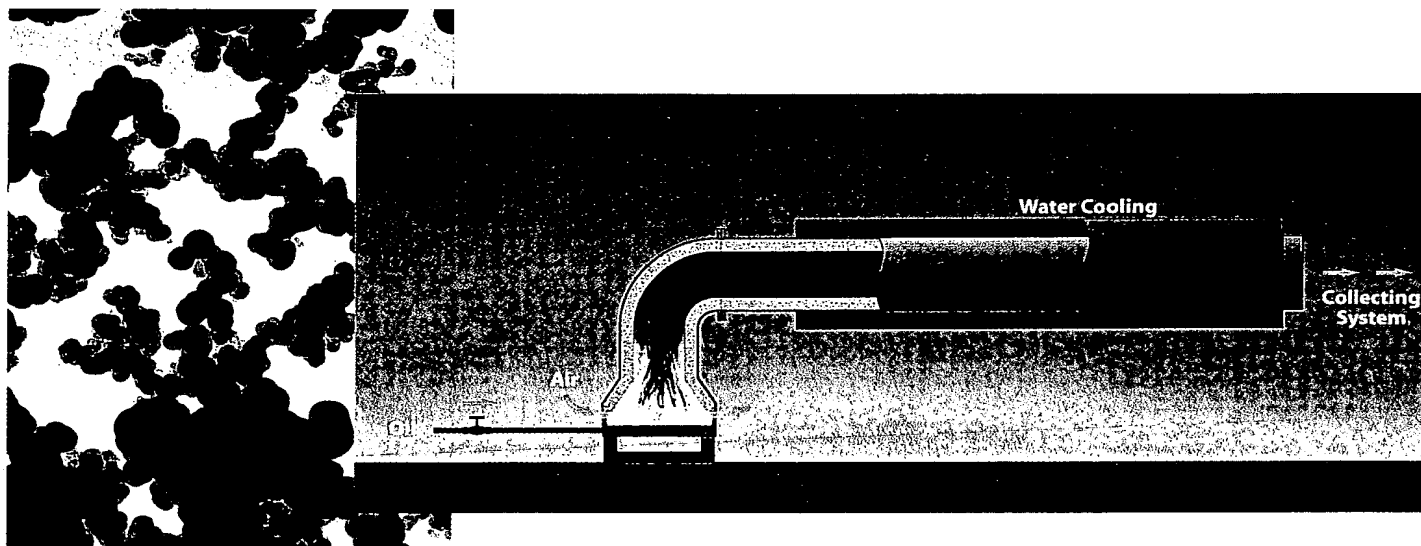
Fig. 11:
*Electron microscope view of lampblack particles.*

Fig. 10:
Scheme of lampblack production plant.

2.2.4 Channel Black Process (historical)

Developed in the United States in the middle of the last century, this carbon black production process is based on the incomplete combustion of natural gas, a resource in which was ample supply at that time. Natural gas flames from a large number of small burners are allowed to impinge on water cooled channels (Fig.12), in a manner similar to the Degussa gas black process. Since the 50s, however, the channel black method continuously lost ground in the rubber industry. Following the oil crisis in the 70s the process was eventually discontinued in the US.
The reason was the limited yield of the raw material (3–6%) as well as the environmental hazard posed by emission of very fine carbon black particles. The thick black smoke billowing from channel black plants, called "hot houses," could be spotted miles away. Also of major importance was the lack of compatibility of channel blacks with the newly emerging synthetic rubber GR-S, now known universally as SBR.

Fig. 12:
Scheme of channel black production process.
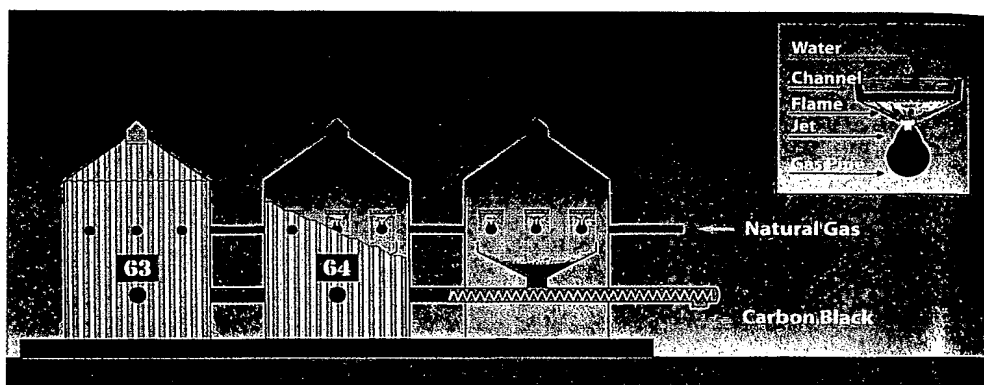
2.2.5 Other Thermal-Oxidative Processes

During the production of synthesis-gas carbon black is formed as a by-product, which has to be separated in a rather complex process. These types of carbon black are characterized by very high apparent specific surface areas, which imparts a unique degree of electrical conductivity to most polymeric materials thus making them useful in the production of conductive and semi–conductive components.

2.3 Thermal Decomposition

This category includes carbon black manufacturing processes such as the thermal black method, the acetylene black method and the electric arc method. The latter is used in large-scale production of acetylene, with carbon black resulting as a by-product. As this particular method is all but extinct, it will not be discussed in greater detail.

2.3.1 Thermal Black Process

This method of producing carbon black is a non-continuous or cyclic process, with natural gas as the most commonly used feedstock, although higher grade hydrocarbons oils are also used. A thermal black plant delivers maximum efficiency when operated in a tandem mode: it consists of two reactors operating alternately in cycles lasting between 5 and 8 minutes, one of which is being heated with a natural gas or oil/air mixture while the other is fed with pure feedstock which undergoes thermal decomposition (Fig. 13).

One could also include the thermal black method in the group of thermal-oxidative processes, with the distinction that energy generation and decomposition reaction are not simultaneous. However, the fact that the actual carbon black formation occurs in the absence of oxygen and at decreasing temperatures, results in carbon black properties that are markedly different from those achieved with thermal-oxidative processes.

Thermal blacks form relatively slowly, resulting in coarse particles in sizes ranging between 300 nm to 500 nm(Fig. 14), referred to as medium thermal. However formerly, when using natural gas only as feedstock, it was possible to dilute it with inert gases and produce a thermal black composed of particles in the range of 120 and 200 nm. This was refered to as fine thermal although it has virtually disappeared from the market.
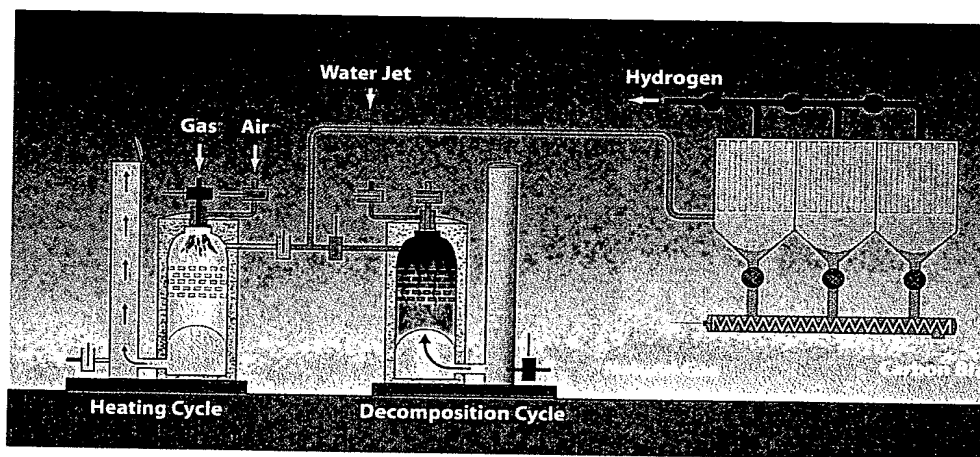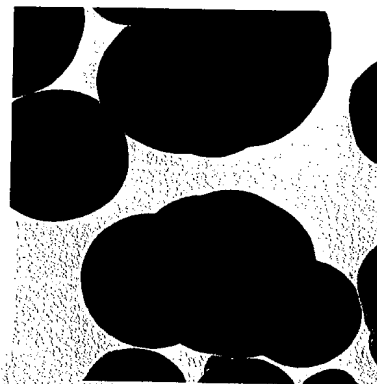
Fig. 13:
Scheme of thermal black production system.

Fig. 14:
Electron microscope view of thermal black particles.
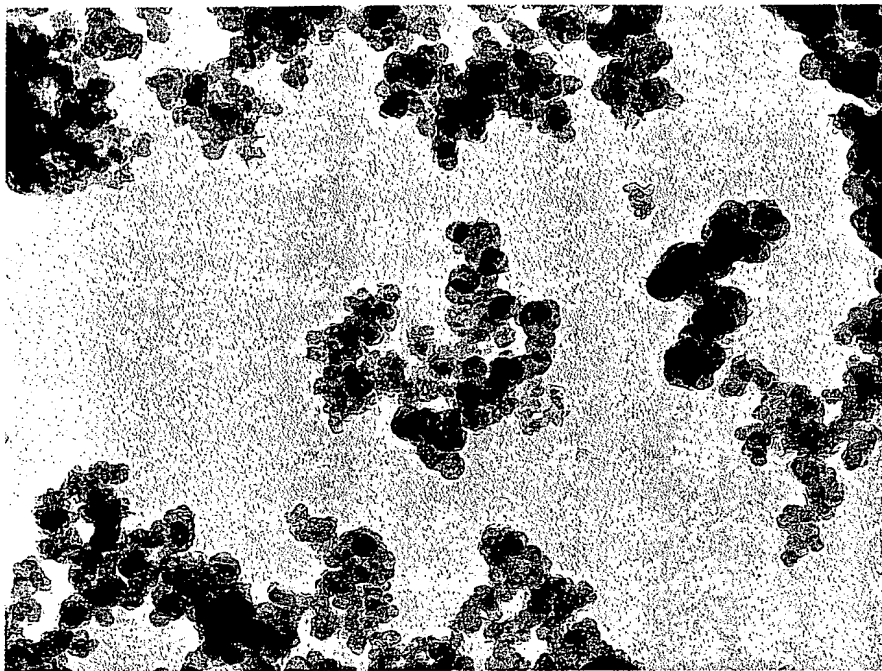
2.3.2 Acetylene Black Process

Fig. 15:
Electron microscope view of acetylene black particles.

At higher temperature, exothermic decomposition of acetylene yields carbon and hydrogen, forming the basis of the acetylene black process. Hydrocarbons are usually added to the acetylene in order to prevent reactor temperatures from rising as a result of the exothermic reaction. Once the reaction mixture has cooled down, the carbon black is separated from the hydrogen.

The way acetylene blacks are created markedly distinguishes them from thermal-oxidative carbon blacks. Although median particle size of acetylene black is in the same range as that of some furnace blacks (30 to 40 nm), the structure diverges noticeably from the spherical form (Fig. 15).

This latter trait makes them ideal candidates for applications in which electrical conductivity plays a role. Their conductivity combined with their highly absorbant nature makes them ideal for use in dry cell batteries.

degussa.

Advanced Fillers & Pigments

Bibliography of Degussa Pigment Blacks and Pigment Black Preparations
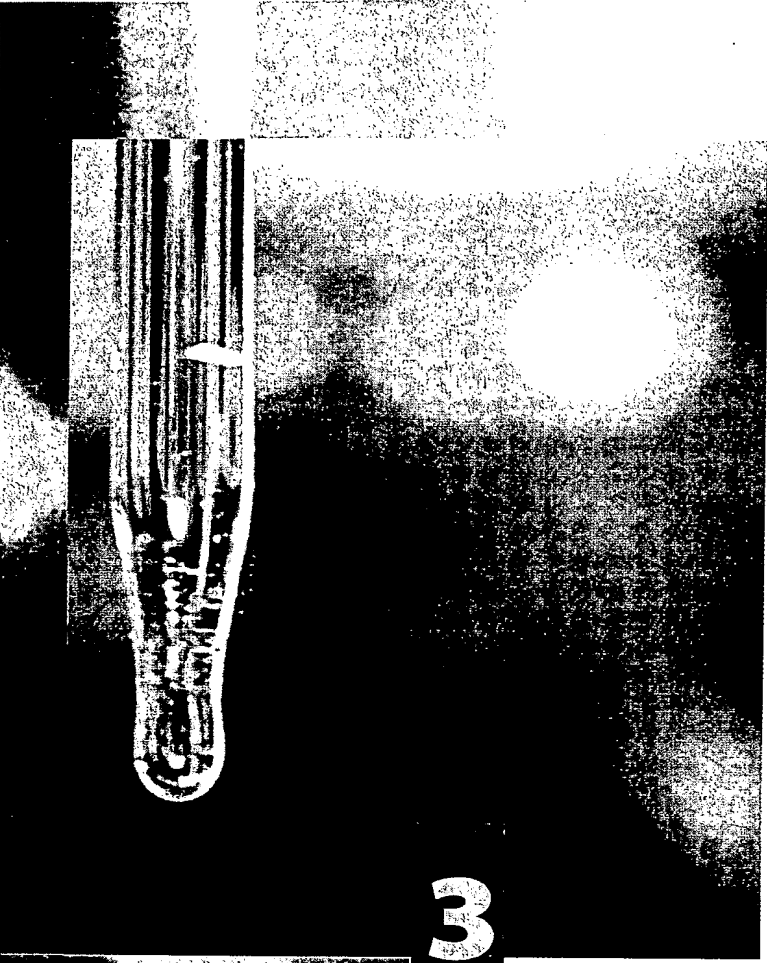
2.4 Carbon Black Dispersions, Compounds, Plastic Masterbatches, Rubber Masterbatches

Carbon blacks can also be delivered to the customer in the form of dispersions which are used to address special dispersibility issues at the customer's site and also keep pollution levels as low as possible during onward processing. Here, a carbon black is dispersed in a variety of liquid and solid media in a wide range of concentrations. The type of carbon black and the base media are usually specified by the customer leading to a wide range of products that fall under the category of carbon black preparations. These compounds are classified based on external appearance (Table 4).

Carbon black compounds	
Aqueous dispersions	Liquid to paste-like products
Pre-dispersions	Powdery products containing water, solvents, wetting agents or softeners
Pastes	Paste-like products containing resins, softeners, wetting agents etc.
Chips	Solids, e.g. carbon black/nitrocellulose compounds
Plastics masterbatches	Granulated concentrates with up to 50% carbon black content
Rubber masterbatches	Carbon black-filled rubber, also in powder form
Oil pellets	Oil-containing granules for printing inks

Table 4: Carbon black compounds.
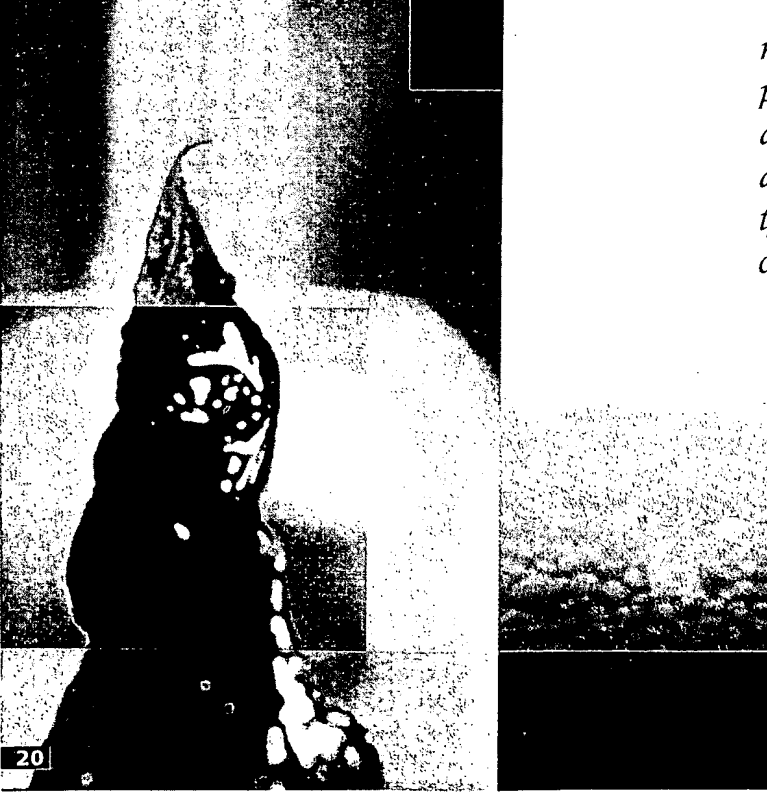
The obvious property of carbon black is no doubt the deep **black color**, perhaps the reason why the adjective is included in the designation in many languages.

Carbon black is classified as a solid and is initially formed as an aerosol, or free-floating particles. This is also why just-formed carbon black has a flaky appearance, and at this stage is referred to as **fluffy** carbon black.

As shown by chemical analysis, non-oxidized carbon blacks are almost pure **carbon**. Nevertheless, using the periodic table designator "C" to describe the product would be misleading and therefore not particularly helpful.

Instead, to characterize this class of materials we must focus on the individual phyical and chemical traits carbon blacks display. Further insights into its properties are only possible after blending the various types of carbon black with the medium chosen for possible applications.

3.1 General Physical and Chemical Properties

The composition described below refer to all carbon black grades, regardless of the production method used. Process-related variances have already been addressed in the description of the various methods in use today for obtaining carbon black. Without the use of photographic image analysis a primary particle of carbon black cannot be seen with the naked eye. Under an optical microscope it takes the tremendous magnifying power of a scanning electron microscope to show that carbon blacks consist of chain-like links or clusters composed of spherical particles, the so-called primary particles.

Fig. 23 depicts an SEM view of a single particle. The formation of spherical, branched aggregates, where the primary particle can have diameters between 10 and 500 nm, is typical of products that develop from the gaseous phase. As we cannot see and measure primary particles without involving expensive equipment and time consuming methods this manifestation of carbon black has led to the

definition of two properties that are of great significance when it comes to characterizing carbon blacks and defining their suitability for specific applications:

- The **specific surface area** (m^2/g) of carbon blacks is a function of primary particle size. Looking at geometric proportions, we can determine that smaller carbon black primary particles have a greater specific surface area.

- The **structure** designates the threedimensional arrangement of primary particles in the aggregate. Extensive interlinking or branching characterizes a "high structure", whereas less pronounced interlinking or branching indicates a "low structure".

A high-resolution electron microscope makes the minutest detail of primary particles visible. This technology, combined with X-ray structural analysis, shows that these primary particles consist of concentrically arranged, graphite-like crystallites. By partially fusing together, the graphite layers are also often twisted into each other, exhibiting a non-ordered state. One single primary particle can contain up to 1,500 of such crystallites.

More recent research using scanning tunnel miscroscopy leads to the supposition that the primary particles consist of superimposed, scale-like layers of graphite. For this reason, the L values determined by X-ray defraction have to be regarded as a median overlap surface of graphite layers and not as the average size of individual crystallites.

Carbon black can thus be considered a highly disorderly form of graphitic carbon. It is by heating the substance to 3000° C under inert

Fig. 23:
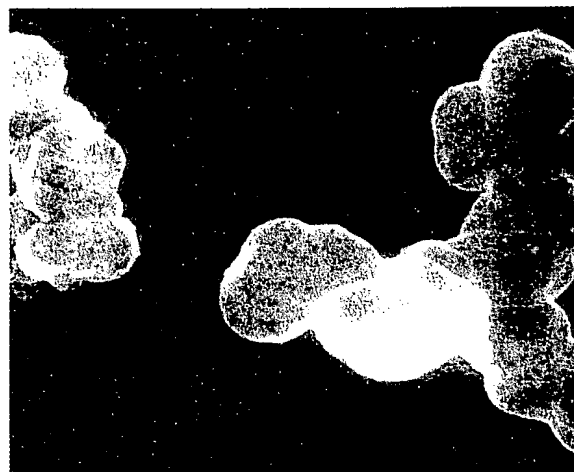*Scanning electron microscope view of a carbon black particle (magnification: x 120,000.)*

Elemental carbon black composition

Element	Content (% of wt.)
Carbon	95 – 99.5
Hydrogen	0.2 – 1.3
Oxygen	0.2 – 0.5
Nitrogen	0 – 0.7
Sulfur	0.1 – 1.0
Residual ash	< 1

Table 5:
Chemical composition of non-treated carbon blacks (approximate values.)

conditions that it develops into an ordered graphitic formation.

Turning back to the chemical analysis, we see that, besides carbon, the elementary analysis of normal carbon black also yields minute quantities of oxygen, hydrogen, nitrogen and sulfur (Table 5). Most of these elements are concentrated on the surface of the carbon black.

Removal of traces of organic elements is possible with the use of special solvents. The carbon black extraction based on toluene, the toluene extract, results in values mostly less than 0.1%. Further analysis of the material shows among other substances, minute quantities of PAHs (polycyclic aromatic hydrocarbons), which are tightly bound to the carbon black surface.

The element of hydrogen is to a certain degree, directly fused to the carbon element. However together with oxygen, another portion forms surface-bound functional groups that can be identified by analysis, both qualitatively and quantitatively. Here, carbonyl, carboxyl, pyrone, phenol, quinone, lactol and ether groups have been identified as the oxygen-containing groups that may be found bound to the surface of the carbon black particle. Heating the substance to 950°C in the absence of oxygen, however, results in separation. This explains their designation as "volatile matter".

Oxygen containing functional groups on the carbon black surface can also be created through specific oxidative post-treatment; oxygen content levels of 15% and higher are possible. These types of carbon blacks are especially suitable for treatment with polar binders.

Sulfur is present in a variety of forms, in its elementary form, as a bound molecule, but also in an oxidized state. High sulfur contents import a certain acidity to industrial carbon blacks.

Nitrogen, when present, is usually contained in the graphite grid. One thing to bear in mind is that sulfur and nitrogen content are contingent primarily upon feedstock type and quality.

Carbon blacks also contain traces of metals, the amounts and type being feedstock dependant. The adjacent table provides an overview of the types of metal and relative content based on Degussa rubber and pigment blacks.

Table 6:
Approximate concentrations of trace metals.

Metals present in carbon black

Element		Content in ppm
Antimony	<	10
Arsenic	<	5
Barium	<	10
Cadmium	<	1
Chrome	<	5
Cobalt	<	10
Copper	<	5
Lead	<	50
Nickel	<	10
Mercury	<	1
Selenium	<	10
Zinc	<	10

Among the **physical properties** of carbon blacks the following two are important:

Density
Though difficult to dermine, it may vary between 1.82 und 1.89 g/cm³.

Electrical conductivity
This aspect is usually not measured in the carbon black itself, but in the compound containing the carbon black, i.e. a polymer or binding agent. Conductivity of a filled polymer increases with the specific surface area and the structure of the carbon black being incorporated into the system. It is also a function of carbon black concentration and dispersion and the type of polymer or binding agent used (Fig. 24).
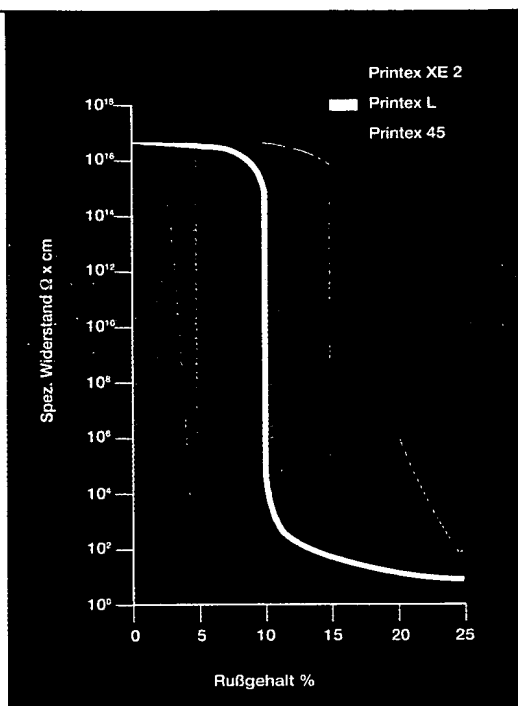

Fig. 24:
Specific volume resistance curves for filled HD polyethylene samples relative to carbon black content.

3.2 Definition

Having described the various processes for obtaining carbon black and product properties, we can narrow down the definition of carbon black as follows:

Carbon blacks are chemically and physically defined products obtained under controlled conditions. Insofar as they are not treated oxidatively, they consist of more than 96% of pure carbon particles and minute quantities of oxygen, hydrogen, nitrogen and sulfur. The negligible amount of organic substances on the surface of the carbon black particle (mostly less than 0.1%) can be extracted using toluene. Metal concentrations are likewise negligible. Primary carbon black particles, ranging from 10 nm to approx. 500 nm in size fuse into chain like aggregates, this defines the structure of individual carbon blacks.

Carbon blacks that are treated oxidatively differ from those that are not in that they may contain up to, and sometimes exceeding, 15 percent oxygen.

Soot (chimney soot and diesel exhaust soot), on the other hand, is a by-product of the uncontrolled combustion of hydrocarbons. Obtaining precise data on the composition of soot is virtually impossible because the conditions under which it is created are fluctuating, precluding any consistency in terms of quality and properties. However, soot can be differentiated from carbon blacks based on inorganic and organic impurity content. Chimney soot, for instance, may have a carbon content of less than 50%, an extract content of more than 15% and an ash content of more than 20%.

3.3 Chemical/Physical Data/Test Methods

For a long time, characterizing carbon blacks was a question of determining different shades of black with the human eye. Precise data on reinforcing effect was available only to a limited degree, in other words, what exactly were the characteristics of a particular carbon black, and what it could be used for were questions that could not easily be answered. In many cases, development of new types of carbon black happened before the characterization of their properties, very much a hit and miss situation.

Following the introduction of the furnace black method, initially there were only a few **basic grades** listed (Fig. 25). It was the discovery in the mid nineteen sixties, that the addition of alkaline metal salts during the production process could be used to influence carbon black structure that was the first major advance that led to a broader typology of furnace blacks.
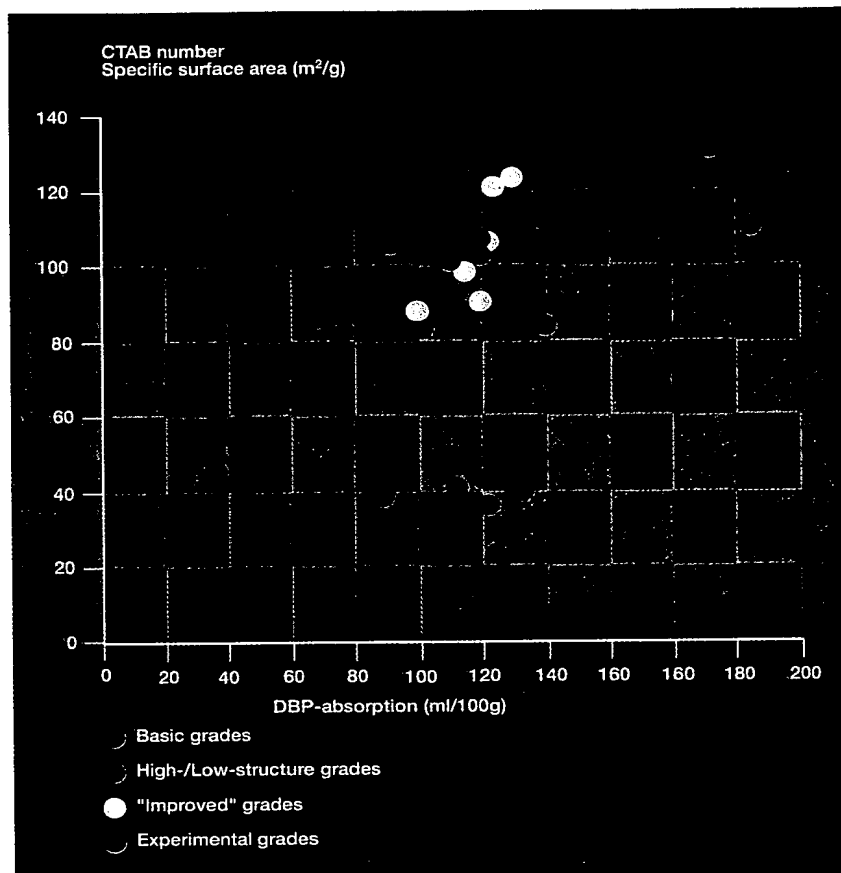

CTAB number
Specific surface area (m²/g)

DBP-absorption (ml/100g)

⌣ Basic grades

⌣ High-/Low-structure grades

● "Improved" grades

⌣ Experimental grades

Fig. 25:
*Evolution of furnace black typology.*

In the 1960s in the field of abrasion-resistantance, **high-structure carbon blacks** began to dominate rubber blacks in tire treads. Determining their structure, however, meant that a quick test method had to be developed. Following a series of comparative tests, DBP (dibuthyl phthalate) absorption ultimately became the preferred tool for determining carbon black structure.

Difficulties arose in the early 1970s when advances in technology led to a new category of reinforcing blacks in furnace black production, the so-called **improved blacks**. What set this new class of carbon black apart from the standard types available at the time was improved abrasion resistance without any apparent change in the iodine number. The differences compared with normal carbon blacks were not easily detectable with the methods available at the time and therefore physical/chemical characterization methods had to be developed in order to establish production parameters which ensured the correct carbon black characteristics were achieved. One of these new methods focused on the determination of porosity of the carbon black surface area.

Further development and refinement of Degussa carbon blacks for the rubber industry has led to nanostructure blacks, which were first introduced in the 1990s. These carbon blacks feature a coarser microsurface in the nanometer range and deliver improved dynamic properties in vulcanized rubber compounds versus comparable ASTM carbon blacks (cf. p. 26).

The development of Purex blacks was another step towards more sophisticated and product orientated carbon blacks. These carbon blacks address the needs of rubber industry for clean and easily dispersible semi-active carbon blacks especially those used in the production of mechanical rubber goods for the automotive industry.

In hindsight, we can say that the development of the electron microscope in the 1940s proved a major milestone in terms of analyzing carbon black and specifying different types for different applications. Where empirical methods used to be the only option for characterizing carbon blacks, this new technology suddenly made it possible to conduct scientific analyses based on particle diameter, particle aggregation and even particle classification in terms of shape and surface details. Interestingly enough, the research showed that virtually no two carbon black particles are exactly alike.
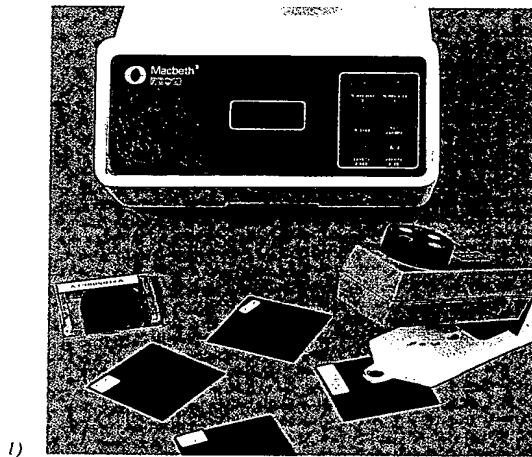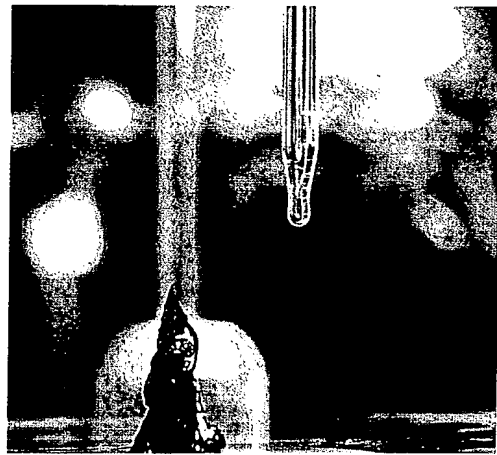
Fig. 26:
Testing methods:
1) Measurement of M_y blackness value;
2) Determination of oil absorption rate.

In a nutshell, all carbon black characterization methods existing today serve to establish **collective** properties, i.e. based on the sum of properties determined for the individual particles. This means we are dealing with a maximum variation of particle properties existing in a range with statistical maximum. It is up to the skilled technician to adjust the peak of the distribution curve at a specific value and define the width of the curve. As long as geometric data is what's being processed and analyzed, the electron microscope is a helpful tool in determining the distribution curve. Other parameters, e.g. conductivity, by contrast cannot be determined for the individual particle.

Fig. 26:
Testing methods
3) Measurement of DPB absorption capability.
4) Measurement of iodine adsorption.

As already pointed out, **average particle size** and **average aggregate size** form the primary characteristic data. However, **particle size distribution** and **aggregate size distribution** are at least as important. As an alternative to lengthy electron microscope analysis a number of methods have been developed to enable quicker characterization as well as allow conclusions for subsequent carbon black applications. While various surface characterization methods have gradually replaced those for particle size determination, aggregate size distribution is now determined via specialized methods such as sedimentation, ultra-centrifugation and light refraction.

Today there is a large spectrum of characterization methods to choose from. One single method for the general characterization of carbon blacks is virtually impossible. It is necessary to specifically adapt identifying methodologies to the various areas of application.
Most **carbon black profiles** are determined based on industry-wide standards which have been developed by the Standard Institute (Deutsches Institut für Normung e.V. – DIN), the International Standards Organization (ISO) and the American Society for Testing and Materials (ASTM). These standards are not only used as a measure by which carbon blacks are characterized, but also as a quality assurance tool for the production process (Table 7a).
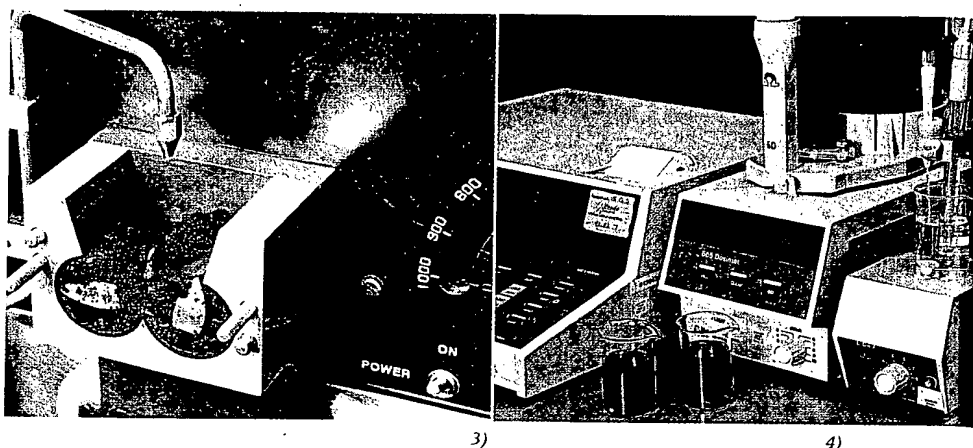
Standardized carbon black typing methods

Description	ISO	ASTM	DIN
Surface			
Iodine adsorption	S-1304	D-1510	53 582
Nitrogen surface	S-4652	D-3037/4820	66 132
CTAB number	6810	D-3765	
Tint-Strength	S-5435	D-3265	
Structure/rheology			
DBP absorption	S-4656	D-2414	53 601
24M4 DBP	6894	D-3493	
Oil absorption	787/5		*)
Coloristics			
Jetness			55 979
Tinting strength	787/16		
	787/24		
Chemical analyses			
Volatile components			53 552
Ash residue	S-1125	D-1506	53 586
Moisture	787/2	D-1509	*)
Sieve residue	787/18	D-1514	*)
Toluene extract			53 553
Toluene discoloration			
Photelometer	S-3858	D-3392	
pH	787/9	D-1512	*)
External appearance/texture and handling properties			
Bulk density	S-1306	D-1513	53 600
Individual pellet hardness		D-3313	
Pellet size distribution		D-1511	

*) DIN-ISO method

Obviously, these methods offer only a glimpse at the comprehensive systems available for testing and evaluating rubber blacks. Special testing methods also exist for carbon black applications in the plastics, coatings and printing inks industries, though we will not further expound on them here.

But what do this carbon black profile figures tell us?

In answer to this question we will describe the main measurement methods in greater detail (cf. Fig. 26).

Table 7a:
Carbon black typing methodology - key profile data.

Table 7b:
Methods for determining in-rubber carbon black properties.

In addition to these carbon black reference profiles, a number of more practical testing methods are being used today, especially for testing rubber blacks in relation to their end use segments. Here, rheometer measurements and the associated RPA have the possibility to become an important tool within the overall framework of testing systems. These tests may be conducted on a standard or production based rubber formulation and are used to establish characteristic, and consistent profile data on the impact of the carbon black in the rubber compound.

Rubber black analysis and testing methods

Rheometric data	D_{max}-D_{min}, $T_{10\%}$, $T_{90\%}$ (Degussa-Hüls Method R 1611)
Modulars 300%	ISO S-3257/ASTM D-3112

3.3.1 Determination of Surface Area

The specific surface area of a carbon black is mainly derived from particle geometry using adsorption methods. Here, iodine adsorption, measured in mg/g is the most common method it prevails over the so-called "iodine surface" method, which is calculated in m^2/g.

Iodine adsorption, a quick test method, requires the carbon black to be dry as surface groups and adsorbed PAHs influence this specification method. For the iodine number to reflect the real surface area it is important that volatile matter make up no more than 1.5 percent of the surface and that the toluene extract be kept under 0.25 percent. This in turn limits this method to furnace blacks with low toluene extractions and lampblacks, and excludes its application to furnace blacks with high contents of solvent-extractable material, gas blacks and oxidized carbon blacks. That is mainly why this parameter is usually not stated when dealing with pigment blacks. This restriction can be circumvented by heating the carbon black to 950° C in a vacuum prior to testing.

The CTAB, absorption, introduced primarily for the characterisation of improved blacks, comes closest to an accurate determination of geometric surface, i.e. pores not included. That is because cetyl trimethyl ammonium bromide (CTAB) has a greater space requirement than nitrogen. This is also why the CTAB number correlates well with particle size, allowing for meaningful predictions on carbon black properties and behavior in the application environment.

Today, gaining increasing importance, is the measurement of surface areas by the **BET multipoint nitrogen absorption** and the **associated STSA (Statistical Thickness Surface Area)**. It has always been recognised that the multipoint nitrogen surface area was the most accurate way of measuring the total surface area of the primary particle, however limitations in equipment did not allow this to become a standard. With the introduction of new automated test equipment it becomes possible to have both the BET multipoint and STSA with a minimum of effort and in a much shorter testing time. It is generally accepted that a combination of these two measurements more clearly defines the surface area of a carbon black allowing for better process control and giving values which relate to the carbon black's performance potential. Ultimately it is predicted that these methods will replace the CTAB absorption.

Conversely, the particle size itself can be used to determine **geometric surface**. This value is obtained from electron microscope photographs which make it possible to measure particle size, determine distribution curves and calculate surface area values. Though a very important tool in the carbon black industry, the method is too time-intensive and complex and the equipment too expensive for obtaining profile data for everyday use.

Tint-strength actually refers to a coloristic parameter: it is the coloring ability of a carbon black as measured against a white pigment (zinc oxide). However, tint-strength is influenced by particle size and structure but also to some extent by particle size distribution. The finer the carbon black particles, the greater the tint-strength, an indirect indicator of surface or particle size specification. On the other hand, a lowering of the structure at the same particle size also correlates with greater tint-strength. Thus tinting strength by itself can often lead to a serious mis-interpretation of the reinforcing capability of a carbon black and should therefore always be viewed in relation to both structure and surface area.

3.3.2 Determination of Structure

The structure of a carbon black particle can only be determined indirectly.
The most commonly accepted method is based on **DBP absorption**. Here, dibutyl phthalate (DBP) is added to a specified quantity of carbon black in a Brabender kneader. The measurement consists of registering the amount of DBP added to reach a predetermined level of torque generated by the kneading machine during titration.

The method is based on the following premise that once all interstices known as void volumes, within the carbon black aggregates are filled with DBP, the surface of the carbon black is considered to be "wetted" and this new surface state will translate into a change in the torque required of the kneading machine. The DBP requirement thus allows for conclusions to be drawn on the degree of aggregation of individual carbon blacks.

The rule: the greater the DBP absorption, measured in ml/100g, the higher the carbon black structure.

Mechanical stress can be applied to destroy agglomerates. This effect is used for determining structure based on the **24M4-DBP** or the **Crushed DBP Absorption** method. Following four repeated applications of pressure, at predefined levels, the DBP absorption of the mechanically stressed carbon black is then measured using a conventional DBP absorption method. As a general rule, 24M4-DBP values are lower than normal DBP values.

Another parameter, carbon black oil absorption, is measured using the so-called flowpoint method. The flowpoint registers the maximum quantity of oil (usually linseed oil) that can be added to a carbon black and still allow for a non-deliquescent cone to form from the mixture. Although the method is not the most accurate, oil absorption is an important indicator in coating applications because a high oil absorption level points to a high binding agent requirement. Carbon black structure, particle size, but most of all density and surface chemistry, all have an effect on oil absorption.

3.3.3 Coloristic Characterization

Jetness refers to the achievable intensity of blackness. The most accurate instrument for measuring what are often very minute differences: the trained eye can differentiate between up to 100 different shades of black. However, a method for measuring residual refraction (< 0,5%) invented by Degussa became a standard as DIN Norm 55 979. Here, a carbon black sample mixed with linseed oil and measured with a spectral photometer results in a M_y-**value**. The finer the carbon black particle, the higher the M_y value (Fig. 27).

A refined version of the paste method described above consists of determining the M_y factor in an alkyde/melamine resin lacquer (PA 1540). The jetness achieved is mapped against various group standards and indicated as a relative blackness value figure M_{yr} for optimum reproducibility and consistency.
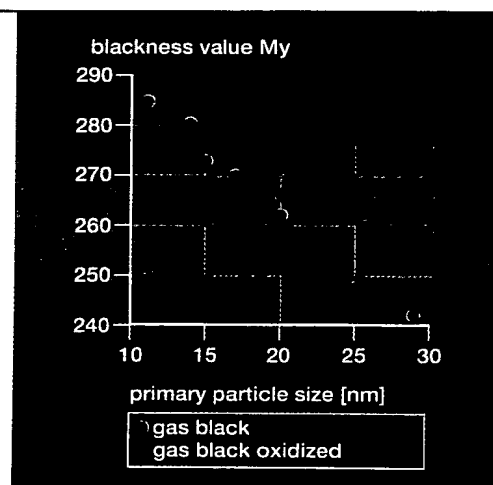
blackness value My

primary particle size [nm]

gas black
gas black oxidized

Fig. 27: Primary particle size and jetness.

29

Tinting strength (as opposed to tint-strength) addresses the ability of a pigment black to darken another pigment. Mixing pigment black with white or color pigments increases the system's light absorption and thus color brilliance. Here, a carbon black paste is mixed with the amount of titanium dioxide required to attain a precisely defined gray tone. This measure is indicated in % relative to a standard carbon black and contingent upon primary particle size and structure. Shade is also dependent on primary particle size and structure, and on oxidation. In the mass tone, fine and high-structured carbon blacks are characterized by a blue hue where coarser carbon blacks have a brownish one. The contrary is the case with gray tones. Shade can be measured spectrophotometrically based on the difference between the shade-specific M_c and the M_y blackness value.

3.3.4 Chemical/Physical Measurements

Volatile matter content gives an indication of the carbon black's oxygen concentration and is determined by heating the carbon black to 950° C. This parameter is especially important for testing carbon blacks that have been post-treated oxidatively.

The ash content points to the level of inorganic impurities coming primarily from the feedstock – iron, calcium and silicon are among the most common. Gas and acetylene blacks are characterized by very low ash content due to their production process.

The sieve residue provides information on particulate impurities which may contain metal or ceramic particles originating from the production unit or coke particles occurring during the production process.

As a result of their high adsorbency, **moisture** is an issue with carbon blacks during storage. High-structure carbon blacks, and in particular oxidatively post-treated carbon blacks, usually are more likely to have elevated moisture content levels.

The **pH** of a carbon black is measured in an aqueous suspension. Untreated carbon blacks have a different pH depending on the process used:
Gas blacks are always acidic because of their oxidized surface. Furnace blacks, on the other hand, are generally alkaline because small quantities of basic oxides are present on the surface. Lampblacks, thermal and in some cases also acetylene blacks are characterized by alkaline to neutral reactions.

Boiling toluene is used to extract organic compounds from the carbon black in a process that takes several hours. The next step is to sublimate the solvent through evaporation and weigh the residue. Analysis of the **toluene extract** shows that, besides aliphatic compounds and sulfur, the carbon black also contains polycyclical aromatic hydrocarbons (PAH). Determining the individual elements in the toluene extract is a time-consuming and complex operation as it involves highly sensitive separation and detection methods. The aggregate toluene extract usually suffices. In the case of rubber blacks, for quick reference the toluene extract method is replaced by toluene discoloration using a spectrometer set for a specific wave length and cold toluene.

3.3.5 Physical Appearance and Handling Properties

The way to determine the space requirement of powder and pelletized carbon blacks is to measure bulk or pour density or compacted or tapped density. Structure is a factor, and in this case high-structure carbon blacks show a lower **bulk density** than low-structure carbon blacks.

In the case of pelletized carbon blacks, **pellet hardness** is a significant parameter of quality as it gives an indication of pellet fragility and hence of the resistance to attrition rate characterized by pellets being destroyed and ultimately ground to dust by friction. While softer pellets make for better dispersion, their inherent propensity towards fines formation may create handling issues. **Pellet size distribution** is a parameter that affects the flow characteristics of pelletized carbon blacks. Uniform pellet size means a lower bulk density, hence ensuring optimum flow behavior.

3.4 Specification, Quality Assurance

Some of the parameters described above are part of the **carbon black specifications** decided on jointly between the customer and the manufacturer. Though these mainly concern surface and structure specifications, they may also address specific requirements as they relate to the carbon black application.

Key parameters are checked at regular intervals during the production process as part of **production control** activities.

One aspect that is important to both manufacturers and users of carbon black is a continued consistency in type and quality and is a direct function of the production process and process control (Fig. 28). **Quality assurance** in terms of product uniformity and reproducibility is at least as important as meeting the customer's individual specifications.

Fig. 28:
Control room at a furnace black plant.

Most manufacturers therefore incorporate **statistical process control (SPC)** in the carbon black production process, a system that builds on universally accepted specifications and guidelines for quality assurance.

The most important target values for individual rubber blacks to ensure optimum production processes were laid down by the American Society for Testing and Materials (ASTM D-1765), e.g. parameters for iodine adsoprtion and DBP absorption (Fig. 29). These parameters are determined at regular intervals throughout the production process. They not only ensure a smooth production process, but also help achieve optimum consistency in terms of end product quality. The "Capability Indices", Cp and Cpk, give an indication of parameter variances and their deviation from target values.
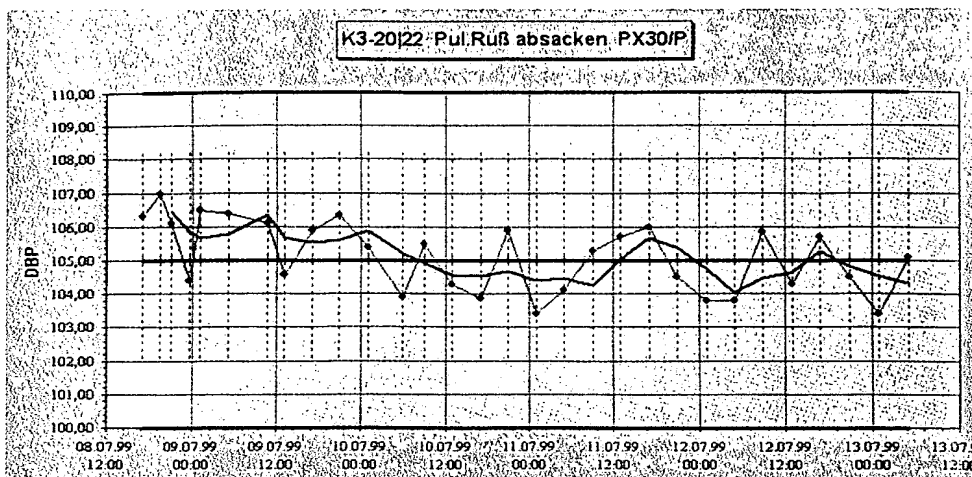
Fig. 29:
Process control chart on the monitor.

3.5 Characteristic Data of various Production Processes

The various production processes for obtaining carbon black all have their advantages and each process is characterized by a certain product range. The key parameters as shown in Table 8 provide an overview of the characteristic data for the main carbon black production processes.

Each process shows a characteristic **primary particle diameter distribution curve.** An electron microscope image of the individual carbon black type is used to determine the quantity and size of the particles, which then yields the number of specific diameter clusters.

Fig. 30 shows the particle size distribution curve for each of the main production methods. Fine carbon blacks (gas blacks), for instance, are clustered in a relatively narrow particle size range. The coarser the carbon black, the flatter the curve.

The type of process also determines the **shape of the primary particles**, as shown when comparing electron microscope images of, for example, furnace black particles with acetylene black particles.
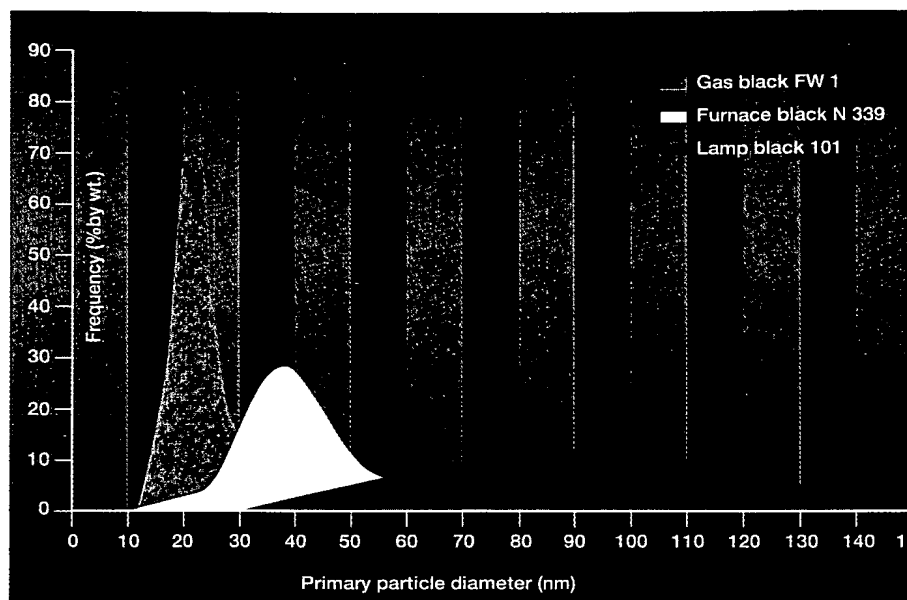

Fig. 30:
Distribution curves for primary particle diameters.

Table 8:
Carbon black variances for different production processes.

Carbon blacks/Production processes

		Thermal-oxidative decomposition		Thermal decomposition		
		Lamp black	Degussa gas black	Furnace black	Thermal black	Acetylene black*
Nitrogen surface	m²/g	16 – 24	90 – 500	15 – 450	6 – 15	approx. 65
Iodine adsorption	mg/g	23 – 33	n. a.	15 – 450	6 – 10	approx. 100
Particle size (arithm. mean)	nm	110 – 120	10 – 30	10 – 80	120 – 500	32 – 42
DBP absorption	ml/100g	100 – 120	n. a.	40 – 200	37 – 43	150 – 200
Oil absorption (FP)	g/100g	250 – 400	220 – 1100	200 – 500	65 – 90	400 – 500
Jetness	M_y	200 – 220	230 – 300	210 – 270	170 – 190	225
Tinting strength		25 – 35	90 – 130	60 – 130	approx. 20	n. a.
Volatile matter	%	1 – 2.5	4 – 24	0.5 – 6	0.5 – 1.0	0.5 – 2,0
pH (**)		6 – 9	4 – 6	6 – 10	7 – 9	5 – 8(*)

(*) Pressureless process
(**) Post-oxidized carbon blacks may register a pH as low as 2
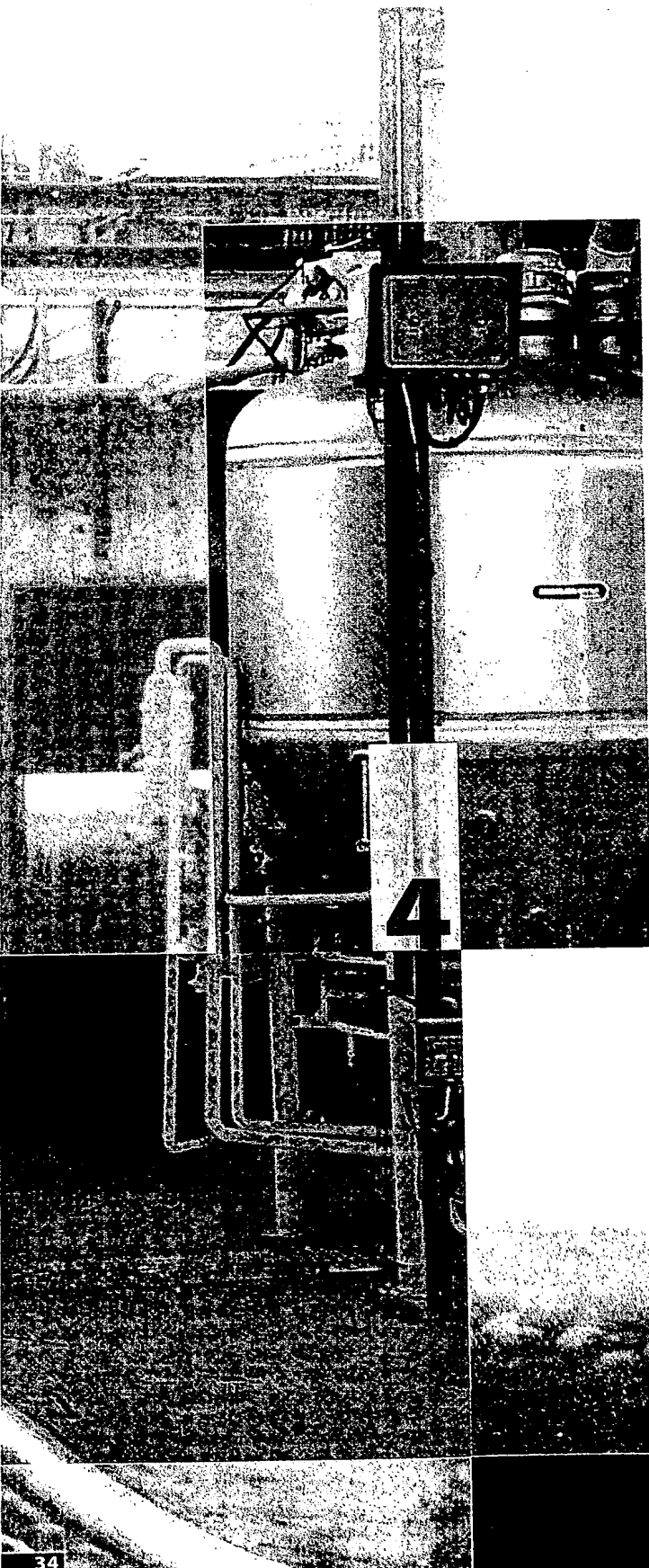
Significant advances have been made in the area of handling and shipping granulated and powdery goods in recent years. New systems for perfectly sealed storage and transportation, in particular, have greatly benefited the carbon black industry.

Carbon blacks are marketed in the form of **powder blacks** (pigment blacks) and **pelletized blacks** (pigment and rubber blacks). The handling systems in some cases differ substantially depending on the type of carbon black for which they are designed.
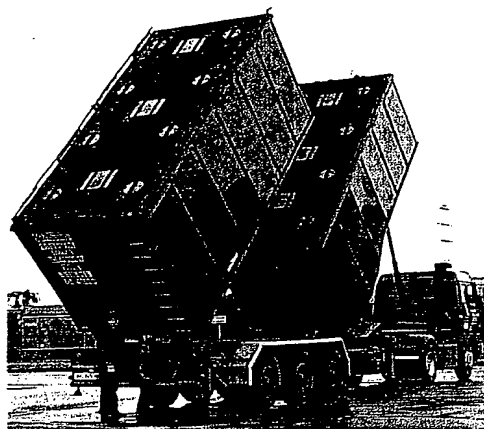
Pelletized carbon blacks, on the other hand, are much easier to handle. Because of their significantly better flow and conveying properties however, the pellet form requires special precautions to prevent the pellets from being crushed during transport. Otherwise, flow characteristics and onward handling may be significantly degraded, with production downtime and equipment failure due to clogging the possible consequence. That is why conveyor belts and bucket elevators are still commonly used for intra-plant carbon black conveying. When pneumatic systems are used it is important to employ low velocity conveying systems (Fig. 31).

One thing to keep in mind is that wet-pelletized carbon black is characterized by a greater pellet hardness than dry-pelletized or oil-pelletized carbon black. Depending on pellet hardness, dense phase conveying systems may damage the pellets. Dune phase and dilute phase systems are not recommended. Short distances are best bridged using screw conveyors, fluid channels or natural frequency conveyors. The transportation of CB in 25 kg bags in the rubber industry is by far the least common. About 85% of the global carbon black is delivered in bulk (road and rail cars) and semibulk container (steal bins, big bags).

Pelletized carbon black destined is available in 25 kg bags, but it is mainly shipped as bulk material in silo trucks and hopper cars. As an additional option FIBC (Flexible Intermediate Bulk Container) and IBC (Intermediate Bulk Container) are used as semi bulk packaging for carbon black. To a very limited extend pelletized carbon black is also shipped in morable storage silos with 26 m³ of volume

Depending on the type, **powder carbon blacks** can more or less easily be fluidized pneumatically. This makes it possible to convey them in large quantities over relatively long distances using high air volumes. Screw conveyors are used mainly for shorter distances.

Due to their low bulk density and relatively poor flow characteristics, **powder blacks** are usually not shipped in rigid vessels or silos, but rather packaged in bags or FIBCs (Flexible Intermediate Bulk Container) as shown in Fig. 32/1.
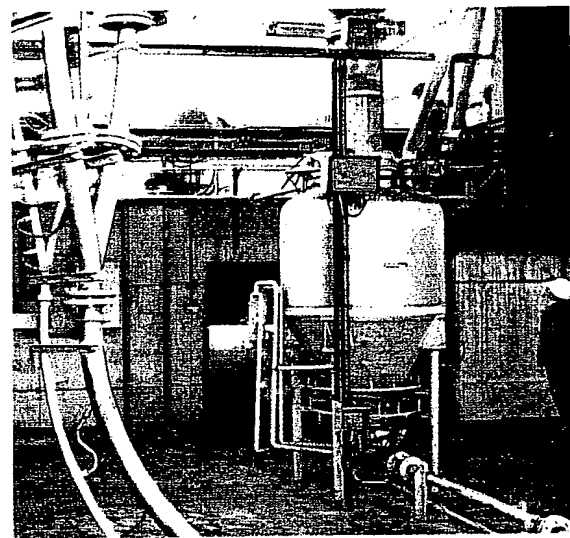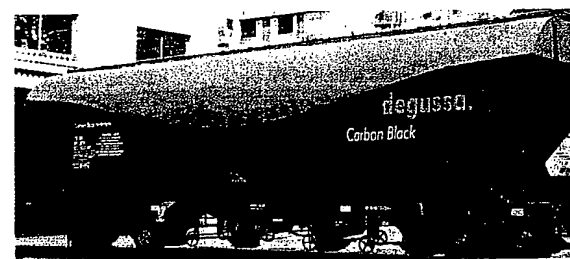
Toxicology

Human experience

In decades of carbon black production and processing using a variety of methods, no significant hazardous effects have so far been registered.

Animal testing results

Acute toxicity : the LD50 acute toxicity rating, oral ingestion by a rat, is above 10,000 mg/kg. Carbon black application on intact skin and on the eye of a rabbit have no irritating effect.
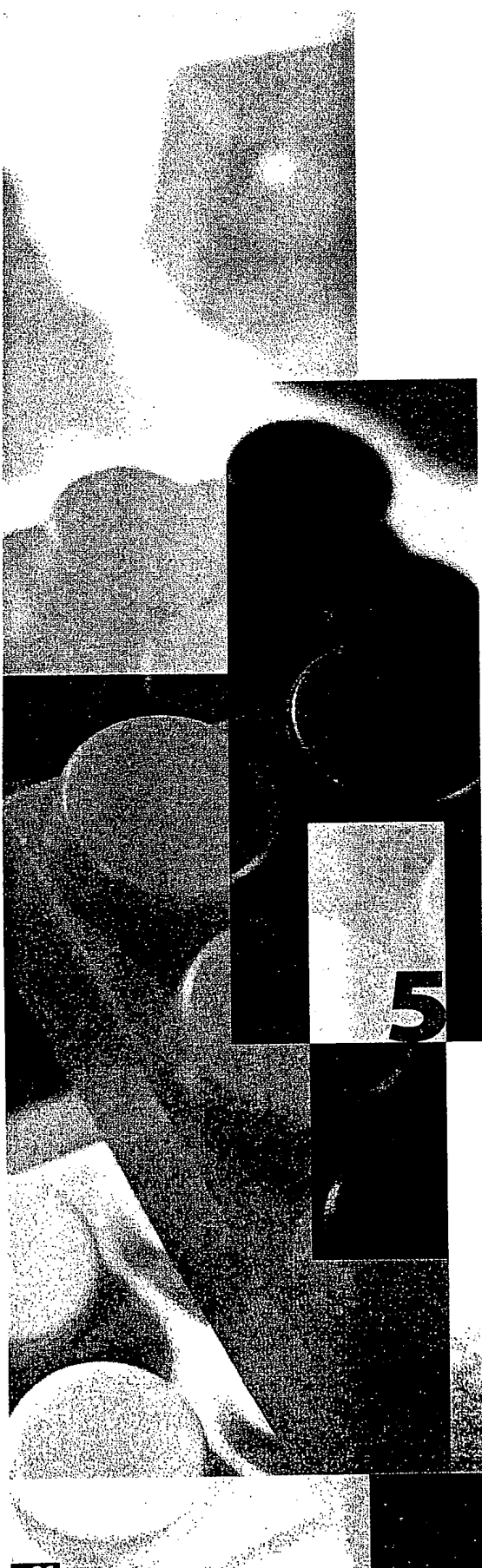
Chronic toxicity

Long-term tracking surveys demostrated that carbon black does not cause harmful effects. In the early 1990s, extended inhalation studies and analyses based on intratracheal instillation indicated a potential for chronic infection, lung fibrosis and tumor development in case of lung saturation with carbon black particles. Here, the significance of the animal species, the fine particle matter and the tumor triggering mechanism has not yet been determined.

In October 1995, the International Agency for Research on Cancer (IARC) reviewed the evaluation of carbon black and recommended an amendment to the rating. As a result, the evaluation of epidemiological data ("inadequate evidence") still applies, though the overall rating was amended from Category 3 to Category 2B ("possible human carcinogen") based on the long-term inhalation study made on rats under conditions of lung overload. As a result of this new evaluation, carbon black is now included in the Danish cancer list and classified as a D2A substance (poisonous and infectious material) in the Canadian Workplace Harzardous Materials Identification System (**WHMIS**) under the Canadian Environmental Protection Act (**CEPA**).

Based on findings by the National Toxicology Program (NTP/USA) as well as European (excluding Denmark) and American legislation regarding chemicals (OSHA), rubber and pigment blacks do not exhibit a mutagenic, teratogenic or carcinogenic potential.

Ecotoxicology

Acute and chronic aquatic organism testing based on fully dissolved carbon blacks is not possible because the substance is insoluble in water.

Carbon black filtrate tests have indicated an LC50 acute fish toxicity and a "No Observed Effect Contraction" value of (NOEC) of > 1.000 mg/l.

In terms of plant life, acute daphne toxicity of carbon black studies indicated an EC50 value of > 5.600 mg/l and a NOEC vaue of 3,200 mg/l. Low pH readings in the range of 4 to 6.5 did have an effect on the values obtained.

Carbon blacks are listed under Reference 1742 as "non hazardous to water quality" in the German list of water pollutants.

Safety-related properties

Under normal application conditions carbon blacks do not display any explosive potential. However, in the presence of significant igniting energy, e.g. a welding torch, carbon black/air mixtures may explode. For this reason, carbon black sources must be removed or hermetically sealed prior to equipment repairs in the vicinity involving welding or equipment generating high operating temperatures.

Carbon monoxide build-up is possible in sealed containers such as silos or in unventilated storage facilities. Here, too, ignition sources should be removed and self-contained air supply systems should be used.

Carbon blacks should be stored under dry conditions. If the "general dust limit" of 6 mg/m³ for fine dust (in Germany) or a concentration of 3.5 mg/m³ for total dust (USA and most European countries) is exceeded, an air suction should be in operation or personnel be required to wear a protective dust mask. Spilled material can be collected to avoid dust build-up, stored in appropriate containers or burned in appropriate firing facilities.

Details on the individual measures regarding safe handling of carbon blacks are described in the relevant material safety data sheets (MSDS).

Special applications

Many carbon blacks fulfill the governmental standards for additives that are used in articles that come into contact with food, drinking water and toys. For more detailed information, please contact the Product Safety Department (SV-FA-PS):

Degussa AG
Rodenbacher Chaussee 4,
DE-63457 Hanau, Germany
Tel.: +49 (0) 61 81 / 59-22 46
Fax: +49 (0) 61 81 / 59-42 05
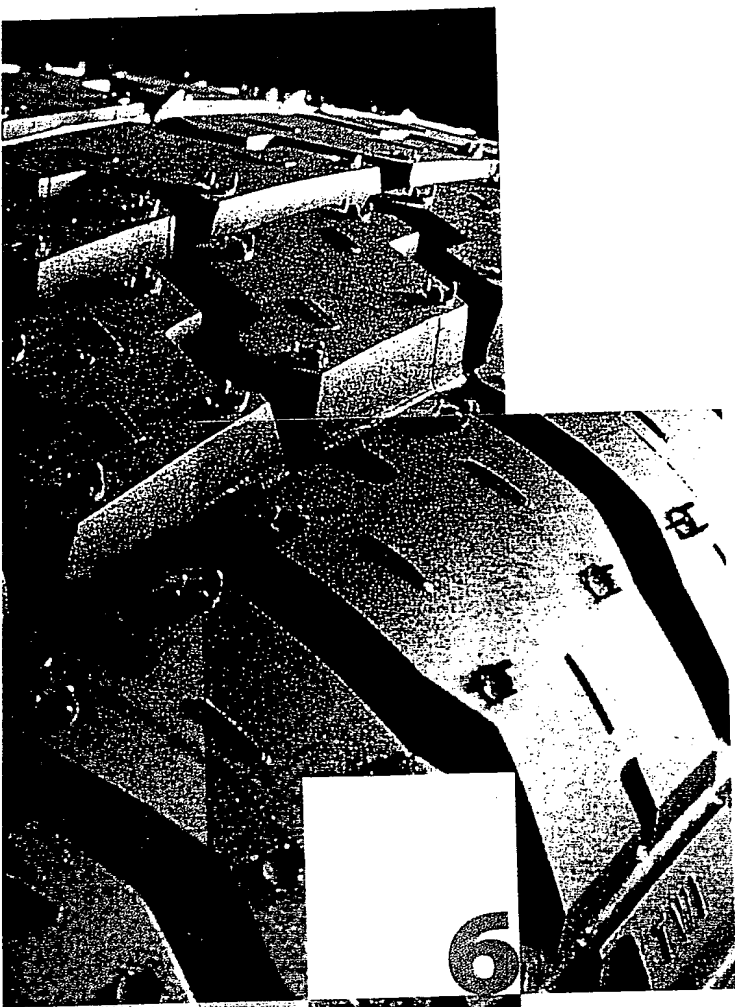
Once you consider its possible uses you will find that there are many answers to the question "What is carbon black?".
Indeed, the physical and chemical properties discussed so far hint at a broad spectrum of applications. The high degree of light absorption, for instance, is one aspect that makes carbon blacks so useful in the coatings, plastics and printing inks industries.
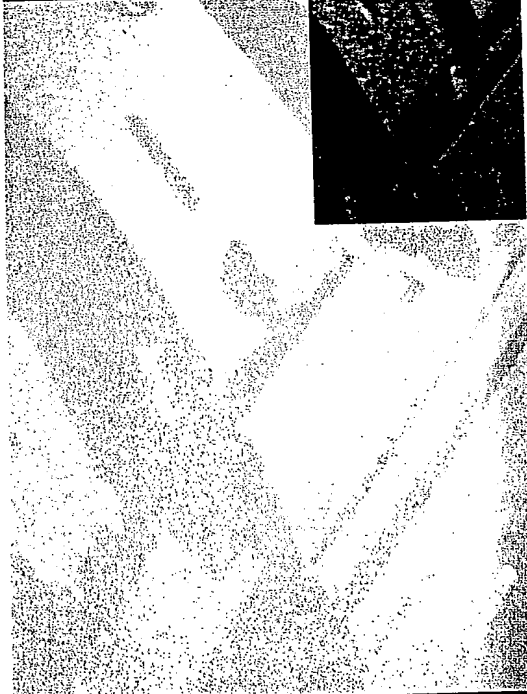
As is the case with graphite, carbon blacks display a certain level of electrical conductivity. That is why special **conductive blacks** are used for conductive or anti-static purposes in rubber and plastics.

Carbon black structure, and surface chemistry after oxidation, affects the viscosity of liquid systems, a fact that is significant to the production of **paints** and other **coatings**.

Primary particle size, aggregate formation and surface activity have led to the most important application for carbon blacks: as a reinforcing agent in rubber. These carbon blacks are most commonly referred to as **reinforcing** or **rubber blacks**.

6.1 Rubber Blacks

The reinforcing effect of carbon black was discovered by accident rather than intentionally shortly after the turn of the 19th century. Until then zinc oxide was the substance of choice for eliminating the inherent stickiness of rubber. The discovery of the reinforcing properties of carbon blacks represented a new dawn for the carbon black, tire and automotive industries. Now tires with improved textile cord could be made to last longer if carbon black was used as a filler in the rubber compound instead of zinc oxide.

However, it took until the early 1920s before carbon blacks were generally used to reinforce tire rubber and other rubber products. Soon it also became clear that there were significant differences between the various types of carbon black, and that these distinctions devolved from processing characteristics and their effect on rubber properties. As a result, new typologies were established, such as MPC = Medium Processing Channel black, or HAF = High Abrasion Furnace black.

The demand for reduced rolling resistance in tires and the introduction of silica/ silane technology in passenger car tire production steered the industry toward a solution for the truck sector. The idea to use a suitable filler to achieve a lower rolling resistance inspired Degussa to develop a new generation of "nanostructure" rubber blacks under the brand name Ecorax®.

In the area of technical rubber components, the main criteria for modern carbon blacks are excellent dispersibility, processing reliability and quality consistency. The Purex® family of carbon blacks developed by Degussa for the MRG-industry addresses these needs.

The following widely acknowledged typology of carbon blacks based on reinforcing properties has stood the test of time:

Active blacks:
High reinforcing capability, fine carbon blacks, tire tread blacks
(particle size: 18–28 nm)

Semi-active blacks:
Lower reinforcing capability, carcass blacks
(particle size: 40–60 nm)

Inactive blacks:
Negligible reinforcing capability, high filling rates
(particle size: > 60 nm)

Though the preceding typology is still widely respected, the internationally recognized ASTM designations are those generally used. The first character in the nomenclature system

for rubber-grade carbon blacks is a letter indicating the effect of the carbon black on the cure rate of a typical rubber compound containing the black. The letter "N" is used to indicate a normal curing rate of typical furnace blacks that have received no special modification to alter their influence on the rate of cure of rubber. The letter "S" is used for channel blacks or for furnace blacks that have been modified usually by oxydative methods, to effectively reduce the curing rate of rubber. Channel blacks characteristically impart a slower rate of cure to rubber compounds. Thus, the letter "S" designates a slow cure rate. Blacks may vary considerably in "curing rate" within each of the two letter classifications. The second character in the system is a 3-digit number the first of which designates the average surface area of the carbon black as measured by nitrogen surface area. The surface area range of the carbon blacks has been divided into six arbitrary groups, and each has been assigned a digit to describe that group. (table 9)

The N 300 series is characterized by a wide variety of rubber blacks, covering no fewer than 10 different types. As mentioned above, fine-particle active blacks are used for rubber components that need to withstand significant levels of mechanical stress, e.g. tire treads.

Semi-active blacks, on the other hand, are used in the tire carcass but also in technical rubber components, from wind, screen seals, and door seals, to floor mats. Tires also contain other special carbon blacks, for instance so-called adhesion blacks for improving radial steel belt adhesion, conductive blacks or inactive blacks for higher filler load rates.
More than 90% of the world's carbon black output goes into the rubber industry, hence the dominant role of rubber blacks.

Table 9:
ASTM rubber black typology
(excerpt.)

Rubber blacks

Designation	Median particle size range (nm)
N 110	11 – 19
N 220	20 – 25
N 330	26 – 30
N 550	40 – 48
N 660	49 – 60
N 770	61 – 100

6.2 Pigment Blacks

Pigment blacks have a number of advantages compared to black organic dyes:
- Color stability
- Solvent resistance
- Acid and alkaline resistance
- Thermal stability
- High hiding power

These carbon blacks are used for a variety of applications in the industries of: printing, (printing inks is not an industry) paints and coatings manufacture, plastics, fiber, paper and construction. That is the reason why they are characterised as **printing blacks, coating blacks or plastic blacks**. But here as well, the industry works with a widely accepted typology based on particle size.

Though not considered an international standard, it serves as the main reference for most manufacturers.

The classification system identifies 4 groups: High Color (HC), Medium Color (MC), Regular Color (RC) and Low Color (LC). The third letter refers to the manufacturing process: (F) for furnace black and (C) for channel or gas black. Finally, oxidative post-treatment is indicated by the suffix (o) for "oxidized."

Pigment blacks

Designation		Range of median particle size (nm)
Gas blacks	Furnace blacks	
HCC	HCF	10 – 15
MCC	MCF	16 – 24
RCC	RCF	25 – 35
	LCF	>36
Gasruße (oxidized)		
HCC (o)		10 – 17
MCC (o)		18 – 24
RCC (o)		>25

Table 10:
Pigment black classification
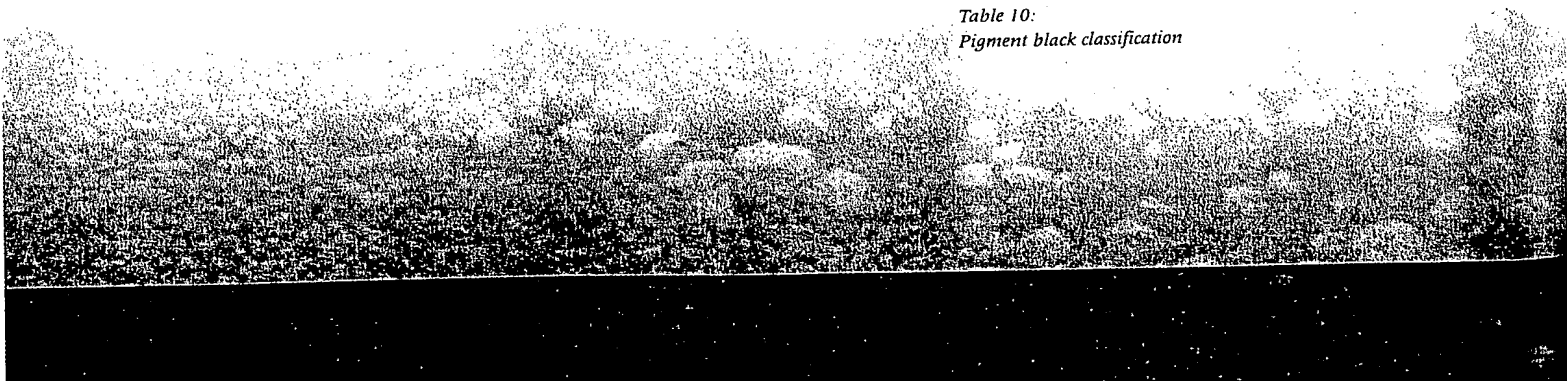
Carbon blacks are not only used as pigment for **printing inks** but also help define the required viscosity for optimum print quality. Here, post-treating the carbon black makes it possible to adapt the substance to the binding agent for optimum system properties.

New pigment blacks being developed on an ongoing basis, are sustaining and driving the pace of innovation in the area of **non-impact printing methods**. Today, pigment blacks manufactured according to the Degussa gas black method are at the fore-front of the industry.

In the **coatings sector**, oxidized, fine particle carbon blacks, are the key to deep **jet black** paints. On the other hand, coarse carbon blacks, the so-called **tinting blacks**, are indispensable for obtaining a desired gray shade or color hue.

Carbon black applications abound in the **plastics industry**. As in the coatings industry, fine-particle types are used for obtaining a deep jet black color. Thanks to its ability to absorb detrimental UV light and convert it into heat, making plastics such as polyole-fines and especially polyethylene, more resistant to UV radiation is also a major merit of carbon black. Anti-static treatment is an important application area as well as is the related field of compounds for power cables. The plastics sector also covers the black pigmentation of synthetic fibers.

The **paper industry** uses carbon blacks with medium-sized particles mainly for decorative and photo-protective products. On the other hand, relatively coarse particles characterize the carbon blacks utilized in the **construction industry**.

Other special application areas, though not focused on the pigmentation properties of these carbon blacks, are also included here e.g. the production of **carbon brushes** and **electrodes**, as well as metal; **metal oxide reduction or molten metal covering systems**, all of which are most suitable for lampblacks.

Though the list of applications is far from being exhausted, the uses described here give a good idea of the impact of carbon black in the world around us.

Without carbon blacks...

... the tires on your car wouldn't provide that extra measure of comfort and safety.

... your morning newspaper would never make it to the breakfast table on time.

... photocopiers might still be mimeograph machines.

... books would simply fade away.

... fashion would miss out on the elegance of a touch of black.

... grand pianos would only come in lighter shades.

... stretch limos would all be white...

Carbon black is one of the basic substances that is indispensable to industry and technology. It comes in many varieties, each one tailored to applications in the most diverse areas. Indeed, carbon black has come a long way and who would have thought that the carbon black would have such a bright future?

NIPex®   IDIS®

Pigment Blacks for
Non-Impact Printing Applications

Professional Series
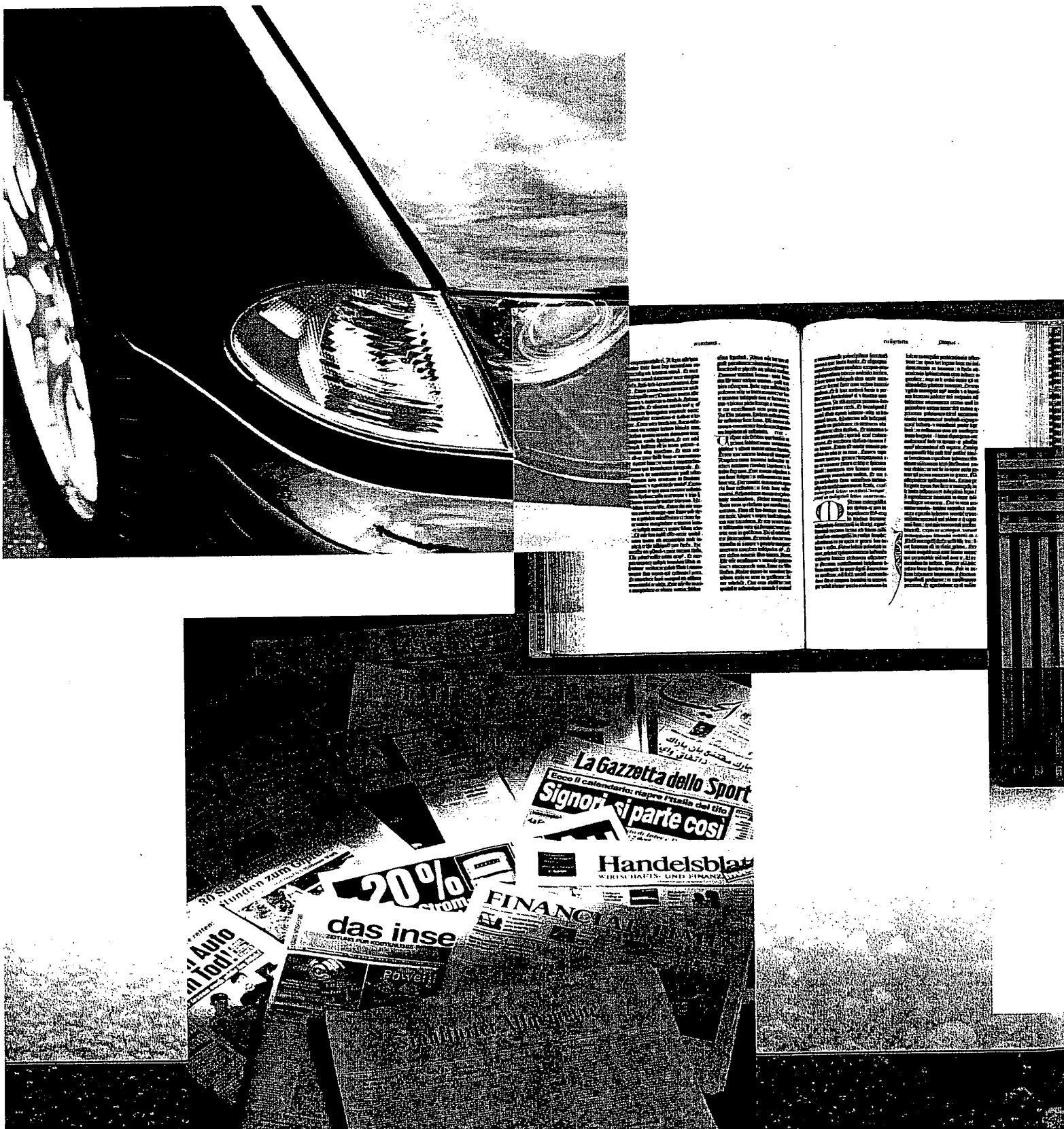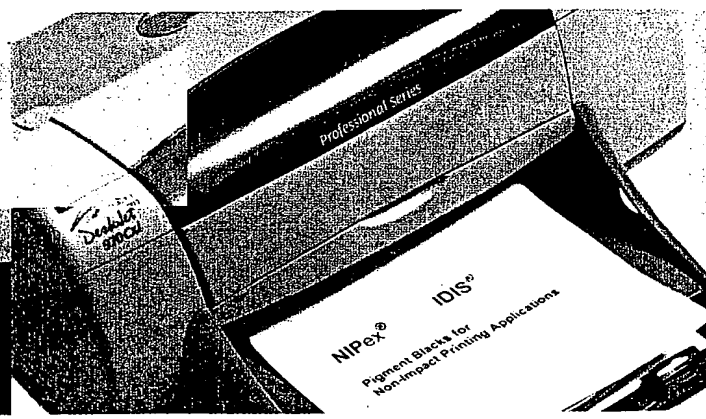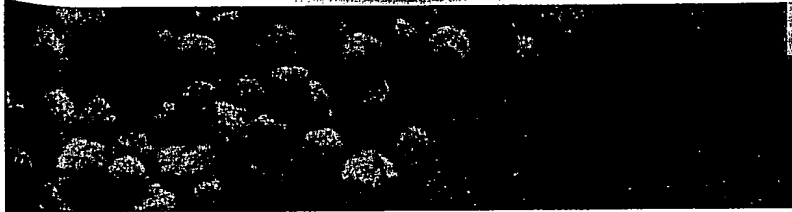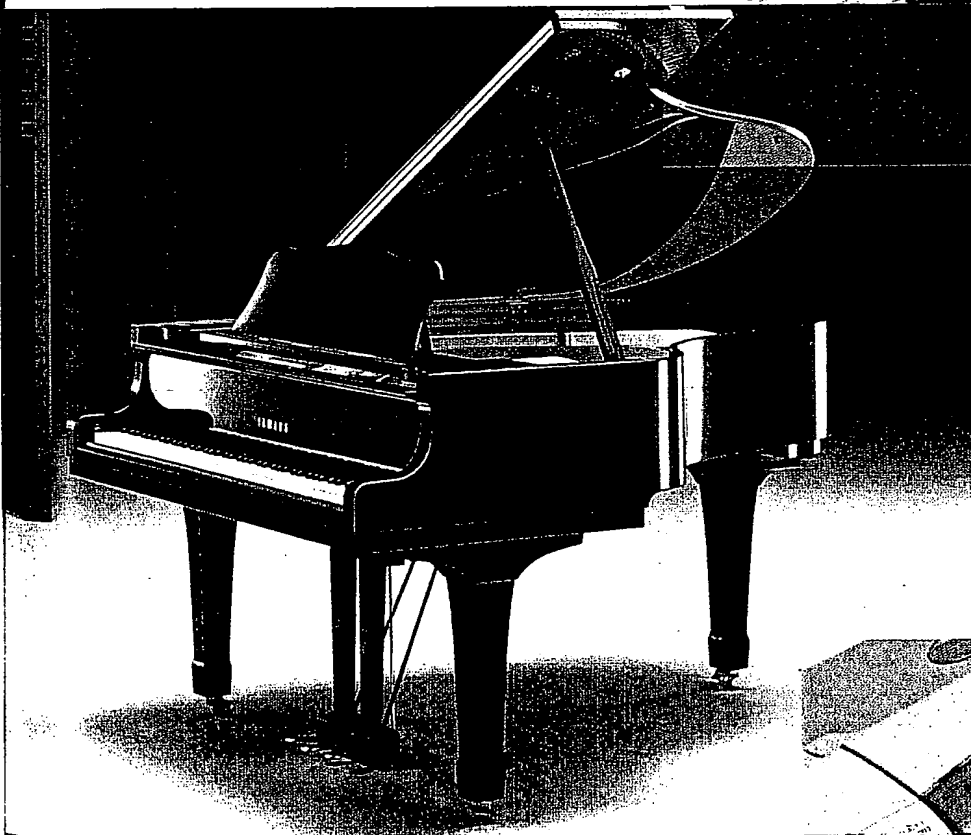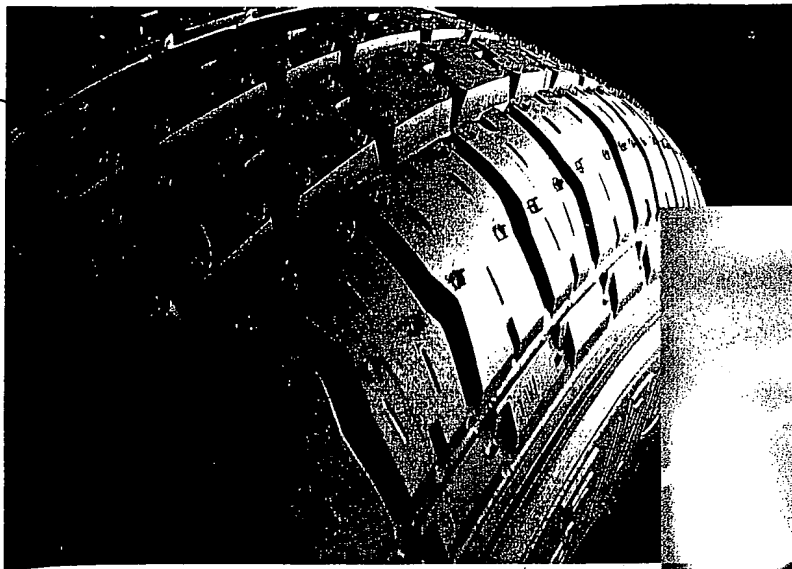
This is the new, revised edition of "What is carbon black?" which has been published in a number of editions over the past 20 years for the information and enjoyment of an ever growing circle of interested readers.

The changes within the industry made an extensive revision necessary. The purpose of this publication is to provide a general insight into the nature and technical aspects of past and present carbon black production processes and applications, including carbon black properties and testing methods. The idea was to provide an engaging overview, not an in-depth discourse. If you are interested in further information, we recommend the literature listed in the bibliography.

In accordance with the general character of this publication, the methods and processes described should not be regarded as blueprints for actual facility design. The information contained herein is based mainly on experience gained at the research labs and production facilities of Degussa or on published materials. Though presented here with the greatest desire for accuracy, the statements contained herein may not be construed as binding with regard to Degussa products and processes as well as their characteristics.

Figure 16:
Copy of a mural painting from Pompeii

Figure 17a:
reproduces a page from the manuscript,
„Harleianus" (9th century A.D.). From the
British Library, Department of Manuscripts.

Figure 17b
The Latin text was taken from the book,
„Vitruvii: De Architectura Libri Decem" by
Valentin Rose, B. G. Teubner-Verlag,
Leipzig, 1899.

Figure 17c:
Translation into English.

Figure 19:
is taken from the Encyclopedia Diderot
(Paris 1770/80), Histoire Naturelle;
Mineralogie, Noir de Fumèe.

Figure 20:
origin unknown

Figure 21, 22a, b:
are taken from the „Neues Handbuch der
Chemischen Technologie", published by
Dr. E. Engler; Vol. V, „Die Fabrikation des
Rußes und der Schwärze" by Dr. Hippolyt
Köhler, 3rd edition, Verlag Friedr. Vieweg &
Sohn, Braunschweig 1912.

Figure of bible on page 42:
With kind permission from the
Gutenberg Museum, Mainz.

Clause for Restriction of Liability

Degussa AG
Business Unit Advanced Fillers
and Pigments
Weißfrauenstraße 9
D-60287 Frankfurt/Main
Tel.: +49-69-2 18-34 28
Fax: +49-69-2 18-30 84
E-Mail:
barbara.merkner@degussa.com
www.degussa-fp.com

FP-26-4-2-0702 TR